

# THE USE OF SODIUM SILICATE FOR THE SIZING OF PAPER

BY  
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TRANSLATED FROM THE GERMAN

WITH A FOREWORD BY

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## FOREWORD

THE decision to publish an English translation, in full, of the original text is, in the first place, justified by the preface to the German edition. It is, in 1922, found worth while to put on record the results of an elaborate investigation extending, with the interruptions of *force majeure*, over a working period of ten years; the subject is rightly judged of sufficient importance to a leading industry, as a permanent contribution to its scientific technical foundations. This will be confirmed by the British papermakers, certainly as a pious opinion. But the opportunity afforded to workers to study, at first hand, and in practical detail, a model experimental investigation involving and illustrating first principles of the paper-making art will have many useful results in carrying on from the stage of opinion to that of conviction. As a model, it will commend itself as a demonstration of both the capabilities and limitations of the well-equipped mill laboratory in solving a problem in manufacturing developments complicated by the many factors involved, and also of the objective spirit and method of inquiry expressed in the aim to arrive at the truth, the whole truth if possible, in any case nothing but the truth. The results recorded must be studied all together, that is, in each section in regard to the particular aims, and then, for the whole matter, integrally, and in relation to the science of colloidal matter, of which the cellulose arts and manufactures afford the most important illustrations, as well as the most attractive prospects of development by discovery and invention.

The results will be found to establish a strong case for the more general adoption of the laboratory method of critical control of the mill operations. For the chemist, with the added qualification of manual craftsmanship in making

sheet samples from prepared stuff, is in the position, all the time, of the navigator of the ship, that is, in regard to routine production; and in regard to competitive invention he is in "wireless" communication with centres of scientific-technical activity all over the world past and present.

The empiric, with a more prejudiced outlook, may be inclined rather to emphasise the limitations of the laboratory method. But the investigator himself is fully aware of these, and in such a way as to express them in exact terms. Moreover, he can critically consider the problem as to the trend of these limitations in respect of the wider outlook.

Thus in the present case: the comparative experiments give results with their own internal evidence of reliability; these establish positive advantages of silicate sizing, and the conditions for optimum results. But always in reference to the scale of the operations and the method adopted, particularly the use of the beater as a mere mixer. In reasoning from the small scale to operations on the mill scale, the time and mass factors require to be evaluated, also the factor of the beating process proper in influencing the interactions of the colloidal components of the "furnish."

It has also to be taken into consideration that the sizing of papers is after all only an auxiliary treatment, and, therefore, of secondary importance to the major operations of preparation of the stuff. In the older technology of paper-making, moreover, the sizing effects were regarded as qualities *added* by way of the agents employed. Since the definite recognition of these effects, together with the whole of the reactions of the papermaking process—from raw material to half stuff, followed by beating preparation, thence to sheet or web of paper—as effects and interactions of colloidal matter, they are regarded as phenomena interdependent with *those* of the components of the fibre substances, which obviously condition the major effects.

Therefore, in applying the results of the brochure, and the author's conclusions to mill problems, the first difficulty to be met is to decide whether the effects established will obtain



on mill-scale operations. The new conditions may obviously determine a greater or lesser realisation.

Thus, as an illustration, the question of news print as a section, and an important one, of printing papers. Since the beating preparation of this furnish is rather of the order of a mixing process and the duration of treatment is relatively short, as in the author's experiments, the data of the brochure should furnish a basis for practical realisation of their results.

On the other hand, (a) the "furnish" replaces 70-80% of the cellulose pulp by ground wood or lignocellulose; and (b) for a laboratory "filtering" operation, in forming the sheet from the beater-mixed "furnish," substitutes a machine operation at high speed, with very large dilution of the stuff by the carrying water with its complement of back water.

It is important thus to set out a critical difficulty which at once confronts the operator. The difficulty in respect of (a) can obviously be resolved in part by an extension of the author's methods to ascertain the relative reactivity of lignocellulose in relation to silicate, including the silica hydrosol and hydrogel.

In regard to (b), the question of fixation and retention of silica or silicates as hydrogels—in union with the relatively "free" fibre furnish—against the draught of the carrying water through the machine wire, is a complex problem. Some of the factors can be studied by laboratory methods, and the results applied to secure the optimum condition of the precipitated hydrogels. But there will remain a "suspense account" in the balance sheet, probably only to be brought down on the right side by persistent systematic study in which the mill becomes for the time a laboratory on the 1000/1 scale.

The purpose of this very slender discussion is merely to point out how the papermaker can take advantage of an investigation such as the present. With long experience it has become increasingly evident to the writer that the exact methods of science and the laboratory are useful and avail-

able up to a point by the craftsman ; and his craftsmanship is strengthened by the study, not supplanted.

But, the craftsman will see further than the laboratory operator in the actual realisation of processes. There is thus a strong case made out to enlist the active co-operation of the craftsmen of the art in extending the scope of the author's investigations and applying the results and data to a wide range of papers.

As a practical example : a mill producing papers of the printings-writings classes, cellulose papers, free from "mechanical" with a preponderating percentage of wood cellulose. It is evident that, taking the fully-beaten "furnish," the effects set out by the author could be realised in the last thirty to sixty minutes before letting down ; that is, the procedure adopted could be applied in the beater, having the roll up, and using it as a mixing machine. It may be presumed that similar effects would be obtained as in the brochure.

But it would appear that silicate added in the earlier stages, that is, at the beginning of beating, might be brought into a definite reacting relationship with the fibre components : thus, in the earliest stage, it is quite clear that the addition of silicate of soda would assist the mere disintegration of the sheets of wood pulp, and also the emulsification of the resin impurity, which may be anything from 0.8 to 1.4 in sulphite pulps. Having got the furnish into uniform mixture, it is quite probable that reactions may continue as between the silicate and the celluloses, especially the hemi-celluloses of the wood cellulose or pulp. In this way a more intimate union may be contracted, and when the component is introduced for the purpose of decomposing the silicate and fixing the silica, a much more intimate union of the silica or silicate may be determined.

Such operations could be done with no disturbance to the mill routine, and if a definite fraction of the furnish were removed at successive periods and specimen quantities made into sheets of uniform weight on the mould, to be afterwards

tested, the progress of the effects could very readily be observed and recorded.

Observation on the draining water from the mould carried out in the laboratory would also give a clear indication of progressive fixing of the silica or silicate. All such observations as stated can be made without any interference with the routine of the mill.

Those mills that are equipped more definitely for investigation, as, for instance, by the provision of a model beater, could determine whether silicate of soda beaten with cellulose pulps in any way contributes to the hydration preparation of the cellulose. This is quite a probable result, in which case the silicate would be a *direct* contributor to paper quality.

If such effects were established it might be possible to make a special mixed colloid by beating together the cellulose pulp and the silicate to more extreme phases of hydration, and use the mixed colloid hydrate as an addition to beaters working on the ordinary lines.

In the next place the relations of silicate to starch could be specially studied. It is already well known that silicate starch mixtures give very characteristic sizing effects in special classes of papers. These effects have only been got by the ordinary procedure by swelling the starch after addition of silicate and using this special silicate starch in the ordinary way, to be fixed by the addition of sulphate of alumina to the usual slightly acid reaction.

There is still another suggestion: there has been, as we all know, endless discussion as to the optimum conditions of efficiency for rosin sizing. It is quite clear that these acid silicates have a special colloidal relationship to the resin colloids, and that mixtures require to be systematically studied both in regard to the ordinary chemical equivalents, and the associated colloidal hydration factors; from which practical results would follow that of employing the silicate in association with prepared sizes.

It is quite evident that these new silicates are a very

economic form of the colloid, and can be made to contribute in various ways to the efficient sizing of papers, which also includes the improvement of the texture of the web or sheet. Other secondary effects, such as the fixation of loading and the more complex effects of fixing colouring matters, are capable of development, the lines of which have been laid down in the brochure under consideration.

C. E. CROSS.

## PREFACE TO GERMAN EDITION

THIS account of an investigation of the action of soluble silicates (water glass) in the sizing of papers is the consolidated publication of sectional articles which have appeared in the *Papierfabrikant*. The work was undertaken on behalf of the German Association of Silicate Manufacturers, and carried out under my direction, with the collaboration of Th. E. Blasweiler, at that time my assistant in the Institut für Zellulosechemie, Darmstadt.

Begun before the war, it suffered a long interruption, to be resumed some time later. Post-war conditions have prevented a more timely publication, but this was decided upon in view of the facts that no publication on the subject had appeared in the meantime, and that the use of silicates in papermaking practice had been considerably extended.

Moreover, the "Verein der Zellstoff und Papier Techniker" had given their imprimatur to the work by the award to the author of the Society's Special Prize.

This deferred publication appears, therefore, to be justified, and will, it is hoped, have a favourable reception at the hands of both papermakers and silicate manufacturers.

EMIL HEUSER.

DARMSTADT, *January, 1922.*



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## INTRODUCTION

As a substitute for rosin size, the cost of which is continually increasing, few of the inorganic colloids are more suitable than the soluble potassium and sodium salts of silicic acid, known technically as water glass. The first experiments on the use of silicates for sizing were made as long as forty years ago, but proved for the most part fruitless, owing to the fact that they were based upon a misconception of the properties of these "inorganic colloids." Klemm, in his paper on "The Mineral Sizing of Printing Paper" (*Wochenblatt für Papierfabrication*, Part 25, p. 1983), made the earliest attempt to obtain a clear idea of the properties of the gels of colloidal aluminium compounds and of their value in relation to what is perhaps the most important class of paper, that used for printing.

The conception of "size-resistance" (*Leimfestigkeit*) has in the course of time become very indefinite. It has been applied too generally in the sense of resistance to the penetration of aqueous inks, even in connection with printing papers, where the idea involved is actually that of resistance to oily liquids or printing varnish, together with the effect of compacting the fibre and filling material in the paper substance.

Klemm, in a circular to the members of the German Papermakers' Association in November, 1907, communicated the practical details of his experimental work on "Mineral Sizing of Printing Paper," and later, in his publication on "The Problem of Rosin Substitutes," before the Congress of the "Verein der Zellstoff und Papierchemiker," in 1909, he recommended mineral sizing for printing paper.

At this time we find the first patent for the application of water glass, by Adolph Franck, of Charlottenburg.

Besides the use of fluosilicates, mentioned in the main patent as the essential feature, the precipitation of fluosilicates by potash and soda glass, or one of these, is claimed in a subsidiary patent. Sizing with fluosilicates will not be dealt with in the present work, since, according to the statement of the patentee, his experiments on this subject were not completed.

In the *Wochenblatt für Papierfabrikation*,\* 1907, Part 35, p. 2868, an anonymous author contributes a paper on the use of the so-called "Heufeld calcined alkaline earth sulphates," whose silicic acid content serves as a filling material and helps to increase the whiteness and glaze of the paper.

Under the heading "Details of Manufacture," another anonymous author (*Wochenblatt*, 1907, Part 52, p. 4234) states that the use of silicate sizing, in conjunction with special furnish and suitable beating of the pulp, prevents the printing paper from becoming too hard.

Klason (*Papierzeitung*, Part 34, p. 1315) used sulphite liquor for precipitating silicate; in this process calcium silicate separates out. The paper was yellowish, but the rattle and surface were improved. These two properties will be discussed by the author in connection with precipitation in the paper as aluminium silicate by means of alum.

In 1911, under the heading "Various Paper-sizing Materials" (*The Papermaker's Monthly Journal*, No. 4, p. 122), it is stated that a cheap size may be obtained by spraying silicate on solid aluminium sulphate, drying and grinding, and using the product in conjunction with rosin.

Two processes characterised by the use of water glass together with rosin for sizing formed the subjects of German patents in 1909 and 1911. The first, by A. Kuldkepp and H. Graf, of Esthonia, claims the intimate mixture of silicate with rosin, casein, or similar bodies at so low a temperature that no silica is precipitated. The second patent, by G. Sommer, of Reval (No. 257,816), depends on the solubility

\* Referred to hereafter as *Wochenblatt*.

of finely powdered or emulsified rosin in cold solutions of bases or basic salts, in particular a solution of silicate.

Both processes will be dealt with in the course of the following work. Mention may be made of the description of the first process in the *Wochenblatt* for 1912, Part 24, p. 2230.

In an Austrian patent assigned to the "Norgine" Chemical Works by Victor Stein, of Aussig-on-Elbe, July 9th, 1911, the use of water-soluble colloids from seaweed, together with an inorganic colloid, is protected.

Ernst Fues (Hanover, December 10th, 1910) filed an application for a patent for "a method of precipitating dissolved colloidal organic substances for paper sizing, etc., depending upon the treatment of the solution with silica compounds in the presence of acids or salts" (*Wochenblatt*, 1913, Part 14, p. 1223). Klemm remarks, in this connection, that silicate sizing had already been successfully applied by him prior to December 10th, 1910.

Fairly complete details of combined starch and water glass effects have been published by Wrede (*Wochenblatt*, 1913, Part 10, pp. 835 ff.). In his method for so-called "mineral-starch sizing" for printing papers, starch and water glass were heated together, and precipitation of the mixed colloid was effected with a large excess of aluminium sulphate. According to Wrede, a loss of from 30-40% of starch occurs in this process, but Fues obtained a practically quantitative precipitation of the colloid by very accurate neutralisation.

For the sake of completeness, mention must be made also of D.R.P. No. 258,181, of Adolph Allihn, for the preparation of art printing papers. In his process boiled starch, in conjunction with alkali silicate, is used as a binder for the pigment, the solution being partially or completely precipitated by acid compounds or other substances capable of precipitating silica. The advantages of papers produced with this sizing over papers coated with casein are, among others, better inking capacity and more even distribution.

of the ink over large surfaces, resistance of the glaze to the pressure of the block, and, above all, so great an absorbing power for ink that no interleaving is necessary.

The possibility of using the purely adhesive action of water glass is indicated in an answer to a correspondent in *Wochenblatt*, 1910, Part 30, p. 2717, on methods for preventing the disintegration of asbestos-cement boards prepared on the cylinder machine.

In Part 45 of *Wochenblatt*, 1913, p. 4250, the possibility of mineral sizing of printing papers with water glass and magnesium sulphate is discussed. The experiments and observations there mentioned will be referred to in the course of the following work.

Under the heading "What many People do not Know," in *Papierfabrikant*, 1915, Part 2, p. 20, an anonymous author recommends the mineral sizing of printing papers with water glass and a certain amount of collidine, after previous treatment with an alumina mordant. Various advantages are claimed for this method.

Still another patent must be mentioned, that of Ernst Altmann (No. 283,751 of February 20th, 1915). In this patent a suspension of talc in gelatine, and in an addition patent (D.R.P. 288,106) the above mixture together with soda is claimed as a size for paper. In the principal patent one of the methods consists in the precipitation of the hydroxides of silica and magnesium contained in a hot suspension of the talc. In the subsidiary patent the method is the precipitation of the alkaline silicate formed from the mineral as an insoluble gelatinous hydrated silica.

This method was one of those attacked in an article, "Rosin Size and its Substitutes," in *Papierzeitung*, 1915, Part 90, p. 1729. The author, however, takes the resistance to writing ink as the full measure of the effect of the sizing, although Altmann and others specifically mention the successful application of the sizing in printing papers.

So much for the most important of the technical records. In view of the importance of mineral sizing and of the circum-

stance that little is known of the reactions which occur in the process, it appeared desirable to subject to an experimental investigation in the laboratory the phenomena of simple mineral sizing and of combined (mineral and organic) sizing, and also to examine the particular practical processes which have been proposed or adopted.



# THE USE OF SODIUM SILICATE FOR THE SIZING OF PAPER

## CHAPTER I

### PURE MINERAL SIZING

SODIUM silicate is commonly known as "water glass," on account of its chemical similarity to ordinary glass. It is actually a glass in which the silicic acid is combined only with an alkali, and not at the same time with an alkaline earth or a heavy metal, and on this account it is easily fusible and soluble in water.

The water glasses of commerce vary in composition from the monosilicate,  $\text{Na}_2\text{SiO}_3$  ( $= \text{Na}_2\text{O}, \text{SiO}_2$ ), to the tetrasilicate,  $\text{Na}_2\text{Si}_4\text{O}_9$  ( $= \text{Na}_2\text{O}, 4\text{SiO}_2$ ).

Before beginning a series of sizing experiments, it was necessary to ascertain the composition of the silicate to be used in the investigation.

ANALYSES OF THE POLYSILICATES USED IN THE WORK.—The analysis of silicate consists in the determination of the silica and total alkali.

(a) *Determination of Silicic Acid.*—Silicic acid is determined by the ordinary gravimetric method of evaporation to dryness in the presence of concentrated hydrochloric acid.

(b) *Determination of the Total Alkalinity.*—The total alkalinity is determined by titration, using methyl orange as the indicator. The original silicate solution of 37° to 40° Bé is diluted approximately 200 times.

The following table gives the results of analyses of the material used in the present work :—

## 2 SODIUM SILICATE FOR SIZING OF PAPER

Sample.	SiO <sub>2</sub> per cent.	Na <sub>2</sub> O per cent.	Ratio SiO <sub>2</sub> /Na <sub>2</sub> O.*
(1) Sodium silicate (Henkel & Co., Dusseldorf) . . .	25.60.	8.06	3.18
(2) Sodium silicate, 38° Bé. solution (van Baerle & Co., Worms). . . . .	26.20	7.91	3.31
(3) Sodium silicate solutions (P. Klaesi)			
(a) . . . . .	14.47	4.35	3.33
(b) . . . . .	15.05	4.38	3.44

From the foregoing analyses it is seen that all four samples lie between the tri- and tetrasilicate, and are not specially prepared substances but the normal commercial product.

In conclusion, there will be given also the composition of a monosilicate which was used in the same way for sizing. This strongly hygroscopic monosilicate, when crystallised with 10H<sub>2</sub>O, is also known as "decasilicate."

	SiO <sub>2</sub> per cent.	Na <sub>2</sub> O per cent.	Ratio SiO <sub>2</sub> /Na <sub>2</sub> O.
Monosilicate supplied by van Baerle & Co., Worms (11° Bé. solution) . . . . .	3.54	3.62	0.98

✓ **SIZING WITH SILICATE.**—The simplest method of carrying out the sizing operation with silicate consists in adding to the paper pulp in the Hollander a given quantity of silicate and, after sufficient mixing, precipitating by the addition of aluminium sulphate ("alum"). The precipitate, consisting of aluminium silicate, is of a colloidal nature, and is adsorbed by the fibres in a state of extreme dispersion. A portion is,

\* Ratio of weights, not molecular ratio.



of course, lost when the pulp is treated on the machine wire, while that part which is retained produces the sizing effect.

It appeared desirable first of all to investigate the reactions when no fibrous matter was present..

**PRECIPITATION WITH ALUMINIUM SULPHATE IN ABSENCE OF FIBRE.**—The first case which required consideration was that of the precipitation of water glass with the best-known size precipitant, aluminium sulphate ("alum"). It was first necessary to find how far the reaction progresses, and also to determine the influence of dilution upon the ease of precipitation; and the behaviour of the precipitate as regards solubility.

The precipitations in absence of fibrous material were carried out at the same concentrations as those employed later in actual sizing experiments. Various quantities of aluminium sulphate were added, to give neutral, weakly acid, acid, and strongly acid reactions respectively (tested with litmus paper).

**I. Neutral Precipitation.**—75 c.c. of silicate solution (van Baerle & Co.), 1 : 5 = 3.930 gm.  $\text{SiO}_2$ , were dissolved in 2 litres of conductivity water, stirred for half an hour, precipitated with 34 c.c. 10% aluminium sulphate solution and again stirred for half an hour. After standing for one hour the liquid, not yet quite clear, was decanted and analysed for  $\text{SiO}_2$ . The flocculation was very slight.

— Took : 3.9300 gm.  $\text{SiO}_2$ .

Found : 3.8065 gm.  $\text{SiO}_2$ .

That is, 96.90%  $\text{SiO}_2$  remained unprecipitated.

**II. Weakly Acid Precipitation.**—The method was the same as before, but 42 c.c. of alum solution were used. The liquid decanted after standing for one hour was still milky.

Took : 3.9300 gm.  $\text{SiO}_2$ .

Found : 3.6904 gm.  $\text{SiO}_2$ .

That is, 93.90%  $\text{SiO}_2$  remained unprecipitated.

**III. Acid Precipitation.**—The method was as before, but

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59 c.c. of 10% alum solution were added, and the decanted liquid was quite clear.

Took : 3.9300 gm.  $\text{SiO}_2$ .

Found : 1.0259 gm.  $\text{SiO}_2$ .

Thus 26.11%  $\text{SiO}_2$  remained unprecipitated.

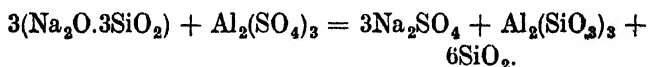
IV. *Strongly Acid Precipitation*.—Method as before. 80 c.c. 10% alum solution were added. The decanted liquid was as clear as water.

Took : 3.9300 gm.  $\text{SiO}_2$ .

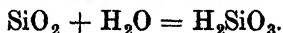
Found : 1.0879 gm.  $\text{SiO}_2$ .

Hence 27.68%  $\text{SiO}_2$  remained unprecipitated.

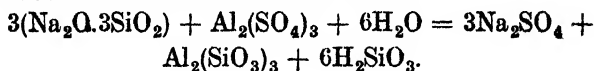
The precipitation of silicate solution by alum, regarded as a chemical process, should proceed according to the following equation :—



The silica may very likely be present, not as  $\text{SiO}_2$ , but as metasilicic acid, according to the equation :—



The course of the reaction would thus be



Stoichiometrically, therefore, 3 molecules of silicate require 1 molecule of  $\text{Al}_2(\text{SO}_4)_3$ .

According to the analysis, 100 gm. of 38° Bé. water glass contain 7.912 gm.  $\text{Na}_2\text{O}$ .

Therefore 15 gm. water-glass solution contain 1.1868 gm.  $\text{Na}_2\text{O}$ . This 1.1868 gm.  $\text{Na}_2\text{O}$  requires 2.185 gm.  $\text{Al}_2(\text{SO}_4)_3$ .

According to the gravimetric analysis, 2 c.c. of the 10%  $\text{Al}_2(\text{SO}_4)_3$  solution contain 0.1013 gm.  $\text{Al}_2(\text{SO}_4)_3$ .

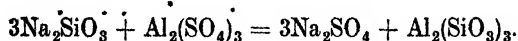
2.185 gm. of  $\text{Al}_2(\text{SO}_4)_3$  are therefore contained in 43.14 c.c. of solution, and 15 gm. of 38° Bé. water glass solution thus require 43.14 c.c. of the 10% aluminium sulphate solution.

Now, it has been shown in the above precipitation experi-

ments that only 34 c.c. of the aluminium sulphate solution are actually required to produce neutrality. The acid reaction corresponding to the difference  $(43.14 - 34) = 9.14$  c.c. of aluminium sulphate solution, is caused by that of the meta-silicic acid  $\text{H}_2\text{SiO}_3$ , and the aluminium silicate  $\text{Al}_2(\text{SiO}_3)_3$  produced in the reaction.  $\text{Na}_2\text{SO}_4$  which is present in the solution is neutral in its reaction.

The explanation for the incomplete precipitation of the silicic acid in the neutral and weakly acid experiments is now evident. In the former, the 34 c.c. of alum solution does not correspond to the amount required for complete reaction, while in the latter, with 42 c.c. of alum solution, the necessary amount  $(45 \text{ c.c.} = 43.14 + 1.86 \text{ c.c. for the 2 litres of water})$  was hardly reached. The silicic acid, therefore, and also the aluminium silicate appear still for the most part as hydrosols in the solution; this explains the milky appearance and the slight degree of precipitation. A small excess of aluminium sulphate over that required by the equation transforms the hydrosols into hydrogels which separate as a flocculent precipitate which settles readily, as shown by the experiments with 59 c.c. and 80 c.c. of alum solution. The fact that the precipitation in the latter case (80 c.c.) is less than in the former (59 c.c.) is to be ascribed to the solubility, small as it is, in acid or strongly acid salt solutions.

In addition to the precipitation of polysilicates, an experiment with the monosilicate was made. The course of the reaction should be in this case as follows:—



According to this equation, 3 parts of  $\text{Na}_2\text{SiO}_3$  require 1 part of  $\text{Al}_2(\text{SO}_4)_3$ . A solution of monosilicate (20 c.c.) containing 0.7164 gm.  $\text{Na}_2\text{SiO}_3$  diluted in the proportion of 1 to 2 was precipitated. According to the above equation 0.6700 gm.  $\text{Al}_2(\text{SO}_4)_3$  is required, i.e., 13.22 c.c. of the empirical 10% solution previously used.

After the addition of 11 c.c.  $\text{Al}_2(\text{SO}_4)_3$  solution, the mixture already showed a neutral reaction to litmus. The

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slight precipitate which was formed settled only very slowly, and the supernatant liquid was milky.

In a second experiment 15.1 c.c. of aluminium sulphate solution (13.22 c.c. + 1.88 c.c. for the 2 litres of water) were added, to give an acid reaction. The precipitate settled quickly, and the liquid was clear.

From these two experiments it is evident, without analysing the liquids, that the aluminium silicate also, which, according to the equation, is the only silica compound formed in this case, has a slightly acid reaction in its hydrosol form. In this case also it is therefore necessary to add aluminium solution until the liquid is decidedly acid, in order to coagulate the aluminium silicate and precipitate it in the form of hydrogel.

The acid action of the aluminium silicate formed in the preceding reaction will now be calculated and expressed as cubic centimetres of the 10% aluminium sulphate solution. We find that 11 c.c. aluminium sulphate solution by gravimetric analysis contain  $0.1013 \times 5.5 = 0.557$  gm.  $\text{Al}_2(\text{SO}_4)_3$ . Further, by the reaction equation, 1 molecule of aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ) corresponds to the formation of 1 molecule of aluminium silicate ( $\text{Al}_2(\text{SiO}_3)_3$ ). We therefore have the relation

$$\text{Al}_2(\text{SO}_4)_3 : \text{Al}_2(\text{SiO}_3)_3 = 342.41 : 283.10 = 0.557 : X$$

$$X = 0.460 \text{ gm. aluminium silicate.}$$

The 0.557 gm. of aluminium sulphate therefore corresponds to 0.460 gm. of aluminium silicate. The 0.460 gm. aluminium silicate in the form of hydrosol has an acid reaction equal to  $(13.22 - 11) = 2.22$  c.c. of the 10% aluminium sulphate solution.

It is further of interest to calculate the acid reaction due to the aluminium silicate and silicic acid produced in the precipitation of the trisilicate; the results are again expressed as cubic centimetres of 10% aluminium sulphate solution. Here again 1 molecule of aluminium sulphate corresponds to the formation of 1 molecule of aluminium silicate.

For the formation of a neutral solution, as mentioned above, 34 p.c. of 10% aluminium sulphate solution were required, containing, according to analysis, 1.722 gm. aluminium sulphate. Here also we have therefore the relation . . . . .

$$\text{Al}_2(\text{SO}_4)_3 : \text{Al}_2(\text{SiO}_3)_3 = 342.41 : 283.10 = 1.722 : X$$

X = 1.423 gm. aluminium silicate.

The experiment on the precipitation of monosilicate has already shown that 0.460 gm. of aluminium silicate in the form of hydrosol has an acid reaction equal to that of 2.22 c.c. of the 10% aluminium sulphate solution. Accordingly, the acid reaction of the 1.423 gm. of aluminium silicate formed in the present experiment is equivalent to 6.87 c.c. of aluminium sulphate solution.

Since now in the precipitation of trisilicate, as above established, an acidity equal to that of 9.14 c.c. of aluminium sulphate was due to the combined effect of the aluminium silicate and silicic acid hydrosols, it is evident that 6.87 c.c. of this is due to the aluminium silicate hydrosol, while the remaining  $(9.14 - 6.87) = 2.27$  c.c. is due to the silicic acid hydrosol.

Summarising briefly the above results, we may say that, in the precipitation of mono- and trisilicates with aluminium sulphate solution, it is necessary to continue the addition of the aluminium sulphate until the solution shows an acid reaction to litmus, since a suitable excess of aluminium sulphate is required to transform into hydrogels the hydrosols of aluminium silicate and silicic acid formed in the neutral solution and to cause them to precipitate.

**EXPERIMENTS ON THE SOLUBILITY OF ALUMINIUM SILICATE PRECIPITATES.**—In view of the great dilution which the mass of silicate-laden fibre undergoes in the paper machine, it appeared desirable to determine the solubility of the precipitates formed by alum and silicate of soda in large quantities of water. Under the conditions obtaining in the process it would be expected that a portion of the precipitate .

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would redissolve, so that a certain loss of the precipitate in the sizing should be taken into account.

In the experiments care has been taken, as far as possible, to choose conditions similar to those under which the sizing itself takes place. Since the dilution at which the actual precipitation is carried out is small in comparison with the volumes of water dealt with in the machine, the precipitation of water glass with alum alone was carried out at relatively slight dilution—namely, 1:6.6—the addition of alum being continued to produce a neutral, acid or strongly acid reaction. In that series of experiments the precipitate was not at first separated from the unprecipitated silicic acid. In the present experiments, which are the first to treat of mixtures containing large quantities of water, only a small proportion of the precipitate calculated as silicic acid was dissolved out, so that the liquid, decanted off from the precipitate as completely as possible, must contain as its chief constituent the unprecipitated silicic acid.

A second treatment of the residue, consisting of the precipitate and adhering liquid, caused appreciable solution of the precipitate. By this decantation process, therefore, the total loss of silicic acid, and also the loss due to the solubility of the precipitate, compared with the amount added in the form of silicate, is obtained. Separate determinations of the silicic acid enabled the various solubilities to be found.

I. *Neutral Precipitation*.—75 c.c. of silicate solution (1:5) were made up to 100 c.c. with distilled water and precipitated with 34 c.c. of 10% alum solution. The whole was then made up to 5 litres with water in a large glass cylinder and stirred mechanically for an hour. After settling, 4 litres of the clear liquid were syphoned off and the silicic acid in this liquid determined. It is clear that the main portion of the silica found in the 4 litres is due to silicic acid which was unprecipitated in the first instance; in addition there is the small amount which has been

redissolved from the precipitate (on the addition of further water).

Used : 75 c.c. silicate (1 : 5), corresponding to 3.930 gm.  $\text{SiO}_2$ .

Found : 0.9698 gm.  $\text{SiO}_2$  in 5 litres = 24.68%  $\text{SiO}_2$ .

The silicic acid content of the 1 litre of liquid and suspended precipitate remaining in the vessel must therefore amount to  $3.9300 - 0.9698 = 2.9602$  gm.

The precipitate was then subjected to another treatment with water, 4 litres of water being added to the residue of 1 litre, bringing the volume again up to 5 litres. After stirring for an hour, 4 litres of clear liquid were again run off and a silica determination made. Here, also, the silicic acid remaining in the 1 litre of the first treatment as well as that in the 1 litre of the second treatment was taken into account.

Used : 2.9602 gm.  $\text{SiO}_2$ .

Found : 0.1506 gm.  $\text{SiO}_2$  in 5 litres of solution.

Therefore the amount of precipitate dissolved is 5.09%, or 3.83% of the amount of  $\text{SiO}_2$  originally used for the precipitation (3.930 gm.).

The total loss in the neutral precipitation is therefore  $24.98 + 3.83 = 28.81\%$ .

II. *Acid Precipitation*.—75 c.c. of silicate solution, 1 : 5, were made up to 100 c.c. and precipitated with 59 c.c. of alum solution to give an acid reaction. The same operations were then carried out as in I. The decanted liquids were now perfectly clear.

Used : 75 c.c. silicate (1 : 5) = 3.930 gm.  $\text{SiO}_2$ .

Found : 0.3805 gm. = 9.68%  $\text{SiO}_2$ .

The precipitate remaining in the 1 litre of liquid, containing  $(3.930 - 0.3805) = 3.5495$  gm.  $\text{SiO}_2$ , was again made up to 5 litres, stirred for an hour and allowed to settle.

\* In order to simplify the calculation, the  $\text{SiO}_2$  content of the 4 litres found by analysis is reckoned in with that of the 1 litre remaining behind.

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The silicic acid was then determined in 4 litres of the clear liquid decanted off.

Used : 3.5495 gm.  $\text{SiO}_2$ .

Found : 0.1274 gm.  $\text{SiO}_2$  in solution.

The amount of silica in the precipitate dissolved is therefore 3.59%, or 3.24% of the  $\text{SiO}_2$  originally taken. The total loss in the acid precipitation is therefore  $9.68 + 3.24 = 12.92\%$   $\text{SiO}_2$ .

III. *Strongly Acid Precipitation*.—75 c.c. silicate solution (1 : 5) were made up to 100 c.c. and precipitated with 80 c.c. of 10% alum solution to give a strongly acid reaction. The further procedure was then as in I. and II. The decanted liquids were quite clear.

Used : 3.9300 gm.  $\text{SiO}_2$  in 75 c.c. silicate (1 : 5).

Found : 0.4658 gm. = 11.85%.

The precipitate remaining in the 1 litre residue, containing  $(3.9300 - 0.4658) = 3.4642$  gm.  $\text{SiO}_2$ , was stirred for an hour in a total of 5 litres of liquid and then allowed to settle. Four litres of the clear liquid were removed and analysed as before.

Used : 3.4642 gm.  $\text{SiO}_2$ .

Found : 0.0229 gm.  $\text{SiO}_2$  in solution.

Therefore the amount of precipitate dissolved is 0.66%, or 0.58% of the  $\text{SiO}_2$  originally used. The total loss in the strongly acid precipitation is therefore  $(11.85 + 0.58) = 12.43\%$   $\text{SiO}_2$ .

A comparison of the solubility experiments with those on precipitation shows that the precipitation is more complete in the concentrated than in the more dilute solutions. Unfortunately, this fact cannot be taken advantage of in the Hollander owing to the great dilution. Further, it is shown that the solubility of precipitates in acid solution is much smaller than in the neutral precipitation. While the solubility of the silicic acid precipitated with a very great excess of alum is smaller than in the case of the (moderately) acid precipitation, yet the sum of the unprecipitated and



dissolved portions is only  $(12.92 - 12.43) = 0.49\%$  lower than in the latter case. Regarded from this point of view the advantage gained by adding a large excess of alum solution would be only slight.

**PRECIPITATION WITH ALUMINIUM SULPHATE IN PRESENCE OF PAPER PULP.**—As an introduction to the present section, a short sketch will be given of the method of carrying out the sizing experiments and taking the samples.

As Alfred Lutz has remarked in his work on "The Influence of Starch on the Properties of Paper" (*Hauptversammlungsbericht der Zellstoff und Papierchemiker*, 1907), it is not possible by drawing samples from the vat to imitate exactly the conditions existing on the paper machine, particularly in respect of the circulation of the machine water. The consumption of sizing material is made to appear more favourable than is actually the case in the machine process owing to the fact that in the drawing of the sample the excess water which passes through the wire flows directly back into the pulp, while on the machine it has usually to be led back by a more or less circuitous pipe system, with the consequent loss of size and filling material. The advantage of laboratory experiments over those carried out in the mill is, however, that a whole series of experiments may be made under constant conditions in order to obtain comparable results. The requirements of the experiments may in such cases be satisfied by the usual sampling process.

The fibrous material used was, with a few exceptions, the "Ia gebleichter Mitscherlich-Zellstoff," of the Aschaffenburg cellulose factory, of Stockstadt-a.-M. This was beaten in a small Hollander of 30 litres capacity at a concentration of from 2.5 to 3.0%. At each fresh charge, samples were taken of the unsized and unfilled pulp, in order to determine the influence of the slight variations in the various batches on handle, rattle, absorbent power, breaking length and stretch of the paper. In connection with the absorbent power, this was tested both for water and printing varnish, so as to obtain an idea of the suitability of the sample for printing.

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In each experiment 2 litres of the pulp, corresponding to 50 gm. of dry substance, were placed in a glass cylinder with stirrer, together with sodium silicate or the mixed solution. The mixture was stirred for half an hour, then precipitated and stirred for another half an hour. The pulp was then filtered on a suction filter through a calico cloth and washed with tap water until the wash water amounted to about 6 litres.

For remarks on the making of the samples, reference should be made to the article in *Papier-Fabrikant*, No. 15, 1921, p. 344, on "The Taking of Samples by Hand in the Laboratory." The method mentioned at the end of that article for the preparation of sheets smooth on one side was employed here.

The sheets were  $17 \times 18$  cm. in size, and the average weight, with a few exceptions, was 100 to 110 gm. per square metre. For the determination of the strength of the paper, three sheets free from faults were chosen, and from each of these three strips were cut across the whole breadth, avoiding the extreme edges. By the method of sampling described in the above paper, and after some practice, the sheets were of such good "look through" and uniformity, that comparable tensile strength measurements could be made. It was of great importance to determine what proportion of the chemicals used remained in the pulp, that is, to estimate the absorption of precipitating material. For this purpose it seemed convenient to consider only one of the components. We, therefore, chose the silicate, or rather the silicic acid used in this form, and the amount absorbed was determined by measurements of the  $\text{SiO}_2$  content of the wash water.

*Expt. 1.*—5% silicate of  $37^\circ$  to  $40^\circ$  Bé. — 1.28%  $\text{SiO}_2$ .

Two litres of pulp, containing 50 gm. air-dried Ia bleached Mitscherlich cellulose, were treated with 25 c.c. 1 : 10 dilute silicate solution (Henkel & Co.) containing 2.5 gm. of silicate of  $37^\circ$  to  $40^\circ$  Bé. The mixture was stirred mechanically for half an hour, and then precipitated with 35 c.c. of 10% alum solution to give an acid reaction. Stirring was then repeated

for half an hour. The amount of alum added, calculated on the air-dried pulp, amounted to 7% of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

The pulp sized in this manner was washed on the filter with tap water until the washings gave no reaction with barium chloride solution. The combined washings, amounting to about 6 litres, were evaporated in a water bath to about 10 c.c., treated with concentrated hydrochloric acid and evaporated to dryness. The silicic acid was in this way determined as  $\text{SiO}_2$ .

In this first sizing experiment, in addition to the  $\text{SiO}_2$  the  $\text{Al}_2\text{O}_3$  was estimated by the usual method of precipitating the boiling solution with ammonia.

*Analysis of Wash Water.*

(a) Silicic Acid.

Used : 2.5 gm. silicate, containing 0.64 gm.  $\text{SiO}_2$ .

Found in wash water : 0.46 gm.  $\text{SiO}_2$ .

Thus 71% of the  $\text{SiO}_2$  appears in the wash water, and 29% in the pulp.

Calculated on the air dried pulp the absorption of  $\text{SiO}_2$  by the pulp amounts to 0.36%.

(b) Alumina.

Used : 0.58 gm.  $\text{Al}_2\text{O}_3$ , according to volumetric analysis.

Found in wash water : 0.03 gm.  $\text{Al}_2\text{O}_3$  (gravimetric analysis).

Thus 5% of the  $\text{Al}_2\text{O}_3$  is in the wash water and 95% in the pulp.

Calculated on the air-dried pulp the absorption of  $\text{Al}_2\text{O}_3$  by the pulp amounts to 1.1%.

The 5%  $\text{Al}_2\text{O}_3$  in the water may arise from the excess of  $\text{Al}_2(\text{SO}_4)_3$  and corresponds to only 1.8 c.c. of the 35 c.c. aluminium sulphate solution added.

*Properties of the Paper.*—Strength : Breaking length 4,480 m., against 4,200 m. for the unsized paper. Stretch almost the same in both cases, about 3.46%.

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Handle and rattle : Better than with the unsized sample.  
Capillary rise in 1 hour at 20° C.

Water : Mean of three readings, 27 mm. Printing  
varnish : Mean, 8.8 mm.

Colour : As white as that of the unsized paper. The experiment shows that only a small proportion of the water glass or silicic acid is retained in the pulp, in spite of the care taken to ensure complete precipitation.

It seemed likely that the use of a larger quantity of silicate and a correspondingly greater amount of alum would lead to better results.

*Expt. 2.*—10% 37 to 40° Bé. silicate — 2.56%  $\text{SiO}_2$ .

The silicate was precipitated with 41 c.c. of 10 per cent. aluminium sulphate solution, i.e., 8.2%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , calculated on the air-dried pulp. The mixture then gave an acid reaction.

The sizing was carried out under the same conditions as in *Expt. 1*.

*Analysis of Wash Water.*

(a) Silicic Acid.

Used : 5 gm. silicate 37° Bé., containing 1.28 gm.  $\text{SiO}_2$ .

Found in wash water : 0.68 gm.  $\text{SiO}_2$ .

Thus 53%  $\text{SiO}_2$  remains in the wash water and 47% in the pulp.

Corresponding with this better yield, the amount of  $\text{SiO}_2$  absorbed is 1.20% calculated on the air-dried pulp, i.e., about four times the value obtained in *Expt. 1*. Nevertheless the characteristics of the paper have only slightly altered.

*Characteristics of the Paper.*—Strength : Breaking length 4,500 m. against 4,200 m. for the unsized paper ; stretch unaltered, 3.40%.

Handle and rattle : Better than for the unsized paper, and also a little better than in *Expt. 1*.

Colour : White as the unsized paper.

Capillary rise in 1 hour at 20° C.

Water : Mean 30.6 mm.

Printing varnish : Mean 8.7 mm.

*Expt. 2A.*—This experiment was carried out with silicate supplied by Kläsi, the method employed being that recommended by him, consisting in a preliminary treatment with alum solution, and addition of the silicate a few minutes before emptying the Hollander. A quantity of silicate was used containing the same amount of  $\text{SiO}_2$  as that in Expt. 2, so that the result of sizing with this sample might be compared with that of Henkel's product.

Two litres of liquid, containing 50 gm. of air-dried pulp, were treated with 41 c.c. of the 10% alum solution, i.e., 8.2%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , calculated on the air dried pulp. The mixture was stirred for half an hour, and 8.54 gm. of silicate solution II. (24° Bé., containing 1.28 gm.  $\text{SiO}_2$ ) were added. The mixture was stirred for another two minutes, and then filtered, washed, and sampled.

*Analysis of the Wash Water.*

(a) Silicic Acid.

Found in wash water : 0.70 gm.  $\text{SiO}_2$ .

Thus 55%  $\text{SiO}_2$  is in the wash water and 45% in the pulp.

Calculated on the air dried pulp this corresponds to an absorption of 1.16%  $\text{SiO}_2$ .

There thus appears to be no essential difference between this and Expt. 2. The characteristics of the paper were the same as in Expt. 2. Since the fraction of  $\text{SiO}_2$  remaining in the pulp was greater in Expt. 2 than in Expt. 1, the properties of the paper being also somewhat better, a further increase in the amount of silicate was tried.

This time silicate from van Baerle & Co. was used. According to the analyses previously given, this contained 7.91%  $\text{Na}_2\text{O}$  and 26.20%  $\text{SiO}_2$ . According to the information supplied by the makers, the product contained 64.55%  $\text{H}_2\text{O}$ , and therefore  $100 - (64.55 + 26.20 + 7.91) = 1.34\%$  is due to impurities (sodium sulphate, traces of sodium chloride;

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iron and alumina). 100 gm. of silicate of 38° Bé. contain therefore

$$\begin{array}{r} 100.00 \text{ gm.} \\ - 64.55 \\ \hline = 35.45 \text{ gm. anhydrous polysilicate and impurities.} \end{array}$$

10 gm. of solid glass are therefore contained in 28.21 gm. of 38° Bé. solution.

A solution of 282.10 gm. 38° Bé. solution was therefore made up to 1,000 c.c. with distilled water, and used for the next experiment.

*Expt. 3.*—10% solid glass = 28.21% silicate solution 38° Bé. = 7.40%  $\text{SiO}_2$ .

The sizing was carried out as in Expt. 2. The pulp was stirred for half an hour with 50 c.c. of silicate solution, containing 5 gm. solid silicate, and precipitation was effected with 55 c.c. of 10% aluminium sulphate solution, i.e., 11%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , calculated on the weight of the air-dried pulp. The solution then showed an acid reaction.

*Analysis of the Wash Water.*

(a) Silicic Acid.

Used : 5 gm. silicate, containing 3.70 gm.  $\text{SiO}_2$ .

Found in the wash water : 1.05 gm.  $\text{SiO}_2$ .

Thus 28%  $\text{SiO}_2$  passes into the washing water and 72% into the pulp.

Calculated on the air-dried pulp the  $\text{SiO}_2$  content amounts to 5.30%.

*Properties of the Paper.*—Strength: Breaking length 4,750 m. against 4,380 m. for the unsized paper. The stretch has risen slightly, from 3.03% for the unsized paper to 3.22%.

Handle and rattle: Better than the unsized sample.

Colour: White, as before sizing.

Capillary rise in 1 hour at 20° C.:

Water: Mean 30 mm.

Printing varnish: Mean 10 mm.

This experiment therefore gave a very much better result than the preceding ones. The assumption that this is due to the use of the chemicals in greater concentration is therefore justified. The increase in strength is not directly proportional, but a proportional increase in strength is not to be expected on *à priori* grounds.

*Expt. 3A.*—In order to test the second sample from Klaesi as to its special suitability for sizing, an Expt. 3A, parallel with Expt. 3, and using the same amount of  $\text{SiO}_2$ , was performed, analogous to 2A. 60 c.c. of 10% aluminium sulphate solution, *i.e.*, 12% of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  calculated on the air-dry pulp, were added and stirred for half an hour.

Shortly before filtration and washing, 25.54 gm. of silicate solution I. of 23° Bé. were added. This amount corresponds to 3.70 gm.  $\text{SiO}_2$ . The wash water was not analysed.

*Properties of the Paper.*—Strength: Breaking length 4,600 m. against 4,300 m. for the unsized paper.

Handle and rattle: As with the sample from Expt. 3.

Colour: White, as in the unsized paper.

Capillary rise in one hour at 20° C.:

Water: Mean 35.7 mm.

Printing varnish: Mean 7.7 mm.

From the results of the experiments on the precipitation of silicate solutions with aluminium sulphate in the absence of paper fibres, and on the solution of the precipitates so formed (*see above*) it seemed desirable to see whether a more complete precipitation, and therefore a greater absorption could be obtained by using a greater excess of aluminium sulphate solution (strongly acid precipitation).

The following experiment was therefore made:—

*Expt. 3B.*—10% of solid silicate = 7.40%  $\text{SiO}_2$  was used. The method of working was the same as in Expt. 3, but 100 c.c. of aluminium sulphate, *i.e.*, 20%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  calculated on the dry pulp, were used, so as to give a strongly acid reaction on precipitation.

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### *Analysis of the Wash Water.*

#### (a) Silicic Acid.

Used : 3.70 gm.  $\text{SiO}_2$ .

Found in the wash water : 1.20 gm.  $\text{SiO}_2$ .

Thus 32%  $\text{SiO}_2$  pass into the water and 68% into the pulp.

This result shows that an excess of the precipitating agents exerts no beneficial effect. Not only is the yield of  $\text{SiO}_2$  no greater, but it is actually about 4% less (68 against 72%). It would appear that in acid or strongly acid salt solutions the precipitated  $\text{SiO}_2$  is soluble, though only to a small extent. For practical purposes, Expt. 3B has no significance, since the amount of  $\text{Al}_2(\text{SO}_4)_3$  used bears no relation to the absorption of silicic acid obtained.

The amount of  $\text{SiO}_2$  taken up, calculated on the air-dried pulp, is 5.00%. Thus, if acid precipitation is chosen for practical use, it is necessary to allow for a loss of about 30% on the silicic acid employed. Part of this loss may evidently be avoided by regeneration and repeated use of the wash water.

**INFLUENCE OF SILICATE SIZING ON THE ABSORPTION OF LOADING BY THE PAPER.**—It was next desirable to determine how far the "adhesive action" of the precipitate of water glass was able to increase the absorption of loading by the paper above that of unsized pulp, or pulp sized by other methods. Both talcum and china clay were added to the paper, the addition being carried out before precipitation with alum.

*Expt. 3C.*—10% solid silicate and 20% china clay.

The method of working was the same as in Expt. 3. After the silicate solution had been added, the loading material was added in the form of a paste, and the mixture stirred for half an hour. The alum solution, amounting to 11%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  on the air-dried pulp, was then added, and the stirring continued for another half-hour. The mixture was then filtered, and washed until the filtrate amounted to 6 litres.



(1) *Absorption of Loading*.—The amount of loading retained in the paper was determined by incineration. The ash due to sizing with 10% silicate solution was estimated on sheets from Expt. 3, and subtracted from the total ash (i.e., ash from silicate sizing + ash from loading material). The loss in weight of the china clay used on heating was also determined, and taken into account in calculating the "absolute quantity of loading," i.e., the actual amount of unheated, air-dried loading. All ash determinations and measurements of loss on heating were carried out in a platinum crucible in a Heræus electric oven. All values are given relative to air-dried pulp (with 65% relative dampness of air).

The following results were obtained :—

Ash from sized but unloaded paper = 2.53%.

Loss of weight of china clay on heating = 13.51%.

Ash from sized and loaded paper = 13.33%.

This 13.33% ash represents 10.80% of ignited loading (since 2.53% is ash due to sized paper).

Allowing for the loss of weight on ignition, this becomes 12.26% of actual china clay, or 61.30% of the clay used.

For comparison with the above, two other samples were prepared, and loaded without being sized. In Expt. 3c' 20% of china clay was added to the unsized pulp, and in 3c'' aluminium sulphate solution was added as well as the filler until the solution showed an acid reaction.

*Expt. 3c'.—20% china clay.*

The clay was added to the pulp in the form of a paste. Stirring was continued for one hour, and the mixture was filtered and washed until the wash water amounted to about 6 litres. Sampling was performed as usual at a dilution of about 1 : 1,000.

An ash determination gave 8.62% ash.

In order to complete the statistics, the ash of the unsized and unloaded paper must first be found.

For this estimation, in order to avoid any source of error, cellulose paper was used which not only consisted of the same raw material, but had also received the same treatment

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with regard to filtering, washing and sampling as the sized and loaded papers.

The cellulose ash found in this way amounted to 0.42%.

The 8.62% of ash from the above paper therefore contained (8.62-0.42%) ignited china clay, *i.e.*  $(8.20 + 1.11) = 9.31\%$  actual china clay (allowing for loss on heating).

Thus 9.31% of china clay, or 46.55% of the amount used, remains in the paper.

*Expt. 3c''*.—20% china clay + 1.8%  $\text{Al}_2(\text{SO}_4)_3 \text{Aq}$ .

The experiment was carried out as before. After half an hour's stirring 9 c.c. of 10%  $\text{Al}_2(\text{SO}_4)_3$  solution were added, to produce an acid reaction, and stirring continued for another half-hour.

An ash determination gave 9.40% ash.

Subtracting from this 0.67%, the value for paper unsized and unloaded, merely made acid with alum, gives 8.83% of ash corresponding to ignited china clay, or  $(8.83 + 1.19) = 10.02\%$  actual china clay.

The paper had therefore retained 10.02% of china clay, or 50.10% of the amount originally added.

RESULTS.—(1) *Retention of Mineral Loading*.—Collecting the various values, we have:—

Sample 3c': Unsized and loaded: 9.31% china clay in the paper = 46.55% of the amount added.

Sample 3c'': Loaded and treated with  $\text{Al}_2(\text{SO}_4)_3$ : 10.02% china clay in the paper = 50.10% of the total.

Sample 3c: Sized and loaded: 12.26% china clay in the paper = 61.30% of the total.

The increase in the retention of loading with the silicate sizing thus amounts to 11% (calculated on the original amount of china clay) over that obtained with paper treated with  $\text{Al}_2(\text{SO}_4)_3$  and 15% over that with totally unsized paper.

(2) *Properties of the Paper*.—Strength: The breaking length of the sized and loaded paper was 3,780 m., and thus reaches practically the same value as that of the unsized and unloaded original material (3,800 m.). Sample 3c'', loaded with clay and treated with alum, shows on the other hand,

as might be expected, less strength than the unsized and unloaded paper, the value being about 1,500 m. A comparison of the figures shows quite clearly that silicate sizing, in addition to its good effect on loading, counteracts the diminution of strength and handle produced by the addition of loading alone.

The stretch of sized and loaded paper was about 1% less than that of the unsized and unloaded paper, the value being about 2.63%.

Handle and rattle were distinctly better in the sized and loaded paper than in that which had been loaded but not sized. The latter was decidedly flabby.

The colour was white, as with the original material.

Capillary rise in one hour at 20° C. :

Water :

C	C'	C''
Mean 46.3 mm.	Mean 40 mm.	Mean 35 mm.

Printing varnish :

C	C'	C''
Mean 9.33 mm.	Mean 6.2 mm.	Mean 7.0 mm.

*Expt. 3D.*—10% solid silicate + 20% talcum.

The method was exactly as in *Expt. 3C*. The "talcum" in paste form was added shortly after the silicate.

(1) *Retention of Loading.*—The loss of weight of the talcum on heating was first determined, and found to be 8.30%.

An ash determination on the sized and loaded paper gave a mean of 16.49%.

The 16.49% of ash corresponds to  $(16.49 - 2.53) = 13.96\%$  of ignited talcum (2.53 is the ash from the sized paper). The actual amount of unignited talcum is therefore  $(13.96 + 1.16) = 15.12\%$ .

The paper thus contained 15.12% of talcum, i.e., 75.60% of the quantity originally used.

For comparison, samples were prepared with talcum alone, and talcum with aluminium sulphate.

*Expt. 3D'.*—20% talcum.

After addition in the form of paste, the mixture was stirred

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for one hour, filtered, and washed until the total washings amounted to 6 litres, when samples were taken.

The ash in the paper amounted to 10.94%, corresponding to  $(10.94 - 0.42)\%$  of ignited talcum (0.42 gm. = cellulose ash), or  $(10.52 + 0.91)\%$  of actual talcum after allowing for loss on heating.

The paper therefore contained 11.43% of talcum, or 57.15% of the amount originally used.

*Expt. 3D*.—20% talcum + 1.8%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

Method as in *Expt. 3C*.

The resulting paper contained 11.94% of ash, corresponding to  $(11.94 - 0.67)\%$  (allowing for cellulose and  $\text{Al}_2(\text{SO}_4)_3$ ) = 11.27% ignited talcum, or  $(11.27 + 0.94) = 12.21$  of unheated talcum.

This represents 61.05% of the amount used.

The paper was considerably firmer than the sample loaded with china clay.

**RESULTS**—(1) *Retention of Loading*.—The collected results are as follows:—

Sample 3D': 11.43% talcum in the paper = 57.15% of the total.

Sample 3D": 12.21% talcum in the paper = 61.05% of the total.

Sample 3D': 15.12% talcum in the paper = 75.60 of the total.

In this case also we find that the fixation for silicate sized paper, calculated from the amount of talcum used, is about 15% higher than that of paper worked with aluminium sulphate, and about 18% higher than that of the unsized paper.

(2) *Characteristics of the Paper*.—Strength: The breaking length of the paper sized and loaded with talcum was about the same (3,610 m.) as that of the original unsized and unloaded material (3,638 m.). Sample 3D" on the other hand, with talcum and alum, showed a diminution of 350 m., from 3,638 m. to 3,280 m. Here also it is seen that the silicate sizing both increases the fixation of filler and counteracts the loss of strength caused by loading.

The stretch remained unaltered at 3.15%.

Handle and rattle were distinctly better with the silicate sized paper than with the paper containing filler only.

The colour was again white, like that of the original material.

Capillary rises in one hour at 20° C.

Water :

3D.	3D'.	3D''.
Mean 34.0 mm.	Mean 32.0 mm.	Mean 29.66 mm.

Printing varnish :

3D.	3D'.	3D''.
Mean 7.66 mm.	Mean 6.0 mm.	Mean 6.66 mm.

Attention may here be called to a phenomenon which has no direct bearing on silica precipitation from silicate solution. In sample 3D'' (talcum and aluminium sulphate) a diminution of strength corresponding to 350 m. of breaking length on that of the unsized and unloaded paper was observed; when china clay was used, although the retention was less, the diminution was 1,500 m. Further, in the case of paper loaded with talcum and sized, the stretch remained unchanged, while loading with china clay diminished this value by 1%. Besides giving a better fixation, talcum therefore also causes an increase in strength, that is, a distinct adhesive action. This may be due to the fact that talcum is present partly as a colloid, like silicic acid hydrosol, in the water. With aluminium sulphate, therefore, a slight precipitation may occur, which has the effect of a slight silicate sizing. In addition, as the experiments of Rohland have shown, the colloidal nature of talcum enables it to adsorb other colloids; an adsorption of hydrated hemi-cellulose which is present to a greater or less extent in the beaten pulp may therefore take place. Both substances would then be precipitated on the fibres by the addition of alum solution. The strengthening qualities of talcum should therefore be ascribed partially to the fixing of the hemi-

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celluloses, and it is necessary to assume that this property is not exhibited by china clay.

As will be seen later, this property of talcum, which is still more evident when the suspension is heated, is effective in fixing in the fibre organic colloids added to it.

**THE SALTING-OUT OF SILICIC ACID.**—The experiments on the precipitation of silicate solution with aluminium sulphate have shown that in the best cases 72% of the silicic acid ( $\text{SiO}_2$ ) used remains in the paper. It is desirable to aim, by using other precipitating agents or methods, at obtaining a better absorption of silicic acid by the paper.

In view of the colloidal nature of solutions of silicic acid, and the strong hydrolytic dissociation of silicate solutions, an absolutely rigid application of the law of mass action is not possible, but from this point of view the salting-out of silicic acid with common salt seemed to be indicated as a feasible method.

(a) *Salting-out of Silicic Acid in Absence of Fibrous Material.*—(1) An amount of silicate corresponding to 3.70 gm.  $\text{SiO}_2$  (according to Expt. 3) was dissolved in 2 litres of tap water. After the addition of only small quantities of common salt a precipitate of silicic acid appeared. Addition of solid salt was continued until no more precipitation occurred from the clear liquor after the precipitate had settled. About 75 gm. of salt were needed for this purpose.

(2) The same quantity of silicate as above was dissolved in 2 litres of tap water, neutralised with hydrochloric acid and treated with solid salt. No precipitation took place. Even when the concentration of salt was raised almost to its solubility limit, no separation occurred.

(3) A solution of monosilicate corresponding to 3.70 gm. silicic acid ( $\text{SiO}_2$ ) was dissolved in 2 litres of water. On treatment with solid salt the first precipitation did not take place until a large amount had been added. It was necessary to add 450 gm. of salt, i.e., six times the quantity necessary with the polysilicate, before the supernatant clear liquid contained no more silicic acid to be salted out.

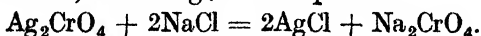
(4) The same quantity of monosilicate was dissolved in 2 litres of water and neutralised with hydrochloric acid. On addition of salt to the limit of its solubility no precipitation could be obtained.

(b) *Salting out of Silicic Acid in the Presence of Pulp.*—A series of sizing experiments was next carried out in order to find how far it was possible to obtain an increased quantity of silicic acid in the pulp by salting out. Since it is evident from the above experiments that we are dealing with a purely physical salting-out action, without any actual chemical reaction, the whole of the salt must be recoverable from the filtrate and washing water.

*Expt. 4.*—10% solid silicate salted out with common salt.

Two litres of pulp, containing 50 gm. of paper, were treated with 56.44 c.c. of 1 : 4 silicate solution, stirred for half an hour, treated with 75 gm. of solid salt, and stirred for a further half-hour. The mixture was filtered, washed and sampled.

*Examination of the Wash Water.*—The wash water, which was alkaline, was analysed for sodium chloride. The volumetric method of Fr. Mohr was used for the estimation; in this method a few drops of potassium chromate solution are added to the chloride, and the liquid is then titrated with normal silver nitrate solution. At the point where the silver nitrate drops into the solution, a red colour forms, due to the presence of silver chromate. This colour disappears on shaking at first, but only until all the alkali chloride has reacted with silver chromate to form silver chloride and alkali chromate, according to the equation



An excess of one drop of silver nitrate now causes the red coloration due to silver chromate to remain permanent.

*Préparation of the Silver Nitrate Solution.*—5 gm. of commercial sodium chloride as used in the above experiments were dissolved in 250 c.c. of water. 50 c.c. of the solution were made up exactly to 250 c.c. 10 c.c. of the latter solution containing 0.04 gm. of salt required 8.40 c.c. of silver nitrate solution. Thus 0.04 gm. NaCl corresponds to 8.40 c.c. of silver nitrate.

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The combined washings from the previous experiment, amounting to about 6,000 c.c., were made up to exactly 6,000 c.c. 50 c.c. of the resulting solution were diluted to 1,000 c.c. in a measuring flask, and 100 c.c. portions of the solution titrated with the standardised silver nitrate solution using neutral potassium chromate as indicator.

Five c.c. of wash water were found to correspond to 13.30 c.c. silver nitrate.

Total NaCl in combined washings

$$= \frac{1,200 \times 13.30 \times 0.04}{8.40} = 76 \text{ gm.}$$

Thus, as expected, all the salt was found in the washings from the sized paper.

Capillary rise in the paper in one hour at 20° C. :

Water : Mean 35 mm.

Printing varnish : 6.66 mm.

The pulp from Expt. 4 was alkaline, which is undesirable in paper making, especially with coloured papers. In Expt. 5, therefore, the mixture was neutralised by the addition of aluminium sulphate after salting out.

*Expt. 5.*—10% solid silicate (in the form of solution) salted out with common salt and neutralised with 8%  $\text{Al}_2(\text{SO}_4)_3$ .

Method as in Expt. 4. After the addition of 75 gm. of salt, 40 c.c. of alum solution were added until the reaction was neutral. After stirring for half an hour the mixture was filtered, washed and sampled. The wash water was milky.

*Examination of the Wash Water :*

(1) *Salt Content.*—The wash water, amounting to 6,200 c.c., was made up to 7,000 c.c. 50 c.c. of this were diluted to 1,000 c.c., and 100 c.c. portions of the latter solution titrated with silver nitrate.

Five c.c. of wash water required : 11.40 c.c. silver nitrate.

Total NaCl in combined washings

$$= \frac{1,400 \times 11.40 \times 0.04}{8.40} = 76 \text{ gm. NaCl.}$$



Here also all the salt was found in the wash water.

(2) *Estimation of Silicic Acid*.—The washings were found to contain 1.48 gm.  $\text{SiO}_2$ .

The amount of  $\text{SiO}_2$  originally added was 3.70 gm., hence  $\frac{1.48 \times 100}{3.70} = 40\%$  of the  $\text{SiO}_2$  passes into the wash water and 60% into the pulp.

Calculated on the air-dried pulp the fixation of  $\text{SiO}_2$  amounts to  $(3.70 - 1.48) \times 2 = 4.44\%$ .

For purposes of comparison we may quote the precipitation of the same quantity of silicate by  $\text{Al}_2(\text{SO}_4)_3$  in 2 litres of water in the absence of fibre. For neutral reaction only 3.1% of the  $\text{SiO}_2$  was precipitated.

*Expt. 6*.—10% of solid silicate (in the form of solution) salted out with common salt and made faintly acid with  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , equivalent to 11% of the weight of dry pulp.

The method was the same as in *Expt. 5*, but after the addition of the salt 55 c.c. of  $\text{Al}_2(\text{SO}_4)_3$  were added, so that the mixture showed an acid reaction. Filtering, washing and sampling were carried out as before.

*Examination of the Wash Water :*

(1) *Salt Content*—determined as before. 75 gm. of  $\text{NaCl}$  were found in the combined washings, so that the whole amount used is again recovered.

(2) *Determination of Silicic Acid*.

Used : 3.70 gm.  $\text{SiO}_2$ .

The washings contained 0.74 gm.

Since the amount originally added was 3.70 gm., 20% of the  $\text{SiO}_2$  remains in the wash water, and 80% in the pulp. The latter figure corresponds to 5.9% on the air-dried pulp.

For the sake of comparison, *Expt. 3* may be mentioned. The same amount of silicate was treated with 11%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  to faint acid reaction. 28% of  $\text{SiO}_2$  remained in the wash water and 72% in the pulp (5.30%  $\text{SiO}_2$  calculated on the air-dried material).

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Capillary rise in one hour at 20° C. :

Water : Mean 42.0 mm.

Printing varnish : Mean 7.0 mm.

The use of common salt with aluminium sulphate has led to an increased fixation of 8%  $\text{SiO}_2$ . The figure, 80% for the  $\text{SiO}_2$  in the pulp, exceeds by 6% the corresponding value (74%) obtained in the precipitation of the same amount of silicate in the absence of fibre.

It was next of importance to try to increase the effect of the alum solution. For this purpose the method was as follows: The pulp was mixed with silicate solution and treated first with aluminium sulphate solution and then with common salt, with the idea that the salt should lower the solubility of the silicic acid precipitate, and also should assist the precipitation of any silicic acid not already thrown down by the alum.

*Expt. 7.*—10% of solid silicate (in solution) precipitated with  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , equal to 16% of the dry pulp, and then treated with salt.

Two litres of pulp, containing 50 gm. of air-dried fibre, were treated with 56.44 c.c. of 1 : 4 silicate solution, stirred for half an hour, precipitated with 80 c.c. of 10% aluminium sulphate solution to a strongly acid reaction, and then further treated with 75 gm. of salt. After a further stirring of half an hour the mixture was filtered, washed and sampled.

*Examination of the Wash Water.*

(1) *Salt Estimation.*—Portions of the wash water were titrated with silver nitrate solution after neutralising with caustic soda.

Five c.c. of wash water required 13.10 c.c. of the silver nitrate solution (see p. 25).

The whole of the wash water therefore contains

$$\frac{1,200 \times 13.10 \times 0.04}{8.40} \quad 75 \text{ gm. NaCl}$$

and the whole of the salt has, therefore, been recovered.

(2) *Estimation of Silicic Acid.*—The washings contained 0.41 gm.  $\text{SiO}_2$ . The amount originally added was 3.70 gm., and, therefore, 11% of the  $\text{SiO}_2$  remains in the wash water, and 89% in the pulp. This corresponds to 6.6%  $\text{SiO}_2$  in the air-dried material.

•Capillary-rise in one hour at 20° C. :

Water : Mean 43.0 mm.

Printing varnish : Mean 7.0 mm.

The good absorption of  $\text{SiO}_2$  in Expts. 6 and 7, confirms the view that the presence of salt makes the precipitate less soluble, besides causing it to come out of solution in a finer form. This view is strengthened by the observation that in the precipitations without fibre a subsequent addition of alum solution to give an acid reaction produced a much finer division of the precipitate after stirring than when no alum was added, or where the solution was not acid.

The results of adding monosilicate to the pulp will next be discussed.

*Expt. 8.*—To 2 litres of pulp, containing 50 gm. air-dried material, 208.6 c.c. of monosilicate solution (1 : 2) were added. The mixture was stirred for half an hour, 450 gm. of salt were added, and the solution was then made strongly acid with 150 c.c. of alum solution. After a further half-hour's stirring the mixture was filtered, washed and sampled. Examination of the wash water showed it to contain 450 gm.  $\text{NaCl}$ . All the salt used is, therefore, recovered.

In order to study the influence of salt and aluminium sulphate, and of salt alone, on the paper, the following experiments were carried out :

*Expt. 9.*—150%  $\text{NaCl}$  + 16%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

• 75 gm. of solid salt were added to 2 litres of pulp, and the mixture stirred for half an hour. 80 c.c. of 10% alum solution were then added and stirring continued for a further half-hour. The mixture was filtered, washed and sampled.

• The total amount of salt used was recovered from the wash water.

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*Expt. 10.*—150 gm. NaCl.

75 gm. of solid salt were added to 2 litres of pulp, containing 50 gm. of dry material. The mixture was stirred for one hour, filtered, washed and sampled.

The wash water contained 75.2 gm. NaCl, the whole amount of salt used being recovered.

In all the sizing experiments in which salt was used, it is seen that the action of the salt is purely mechanical. A "salting-out" action actually occurred also in the pulp, and the experiments further show that cellulose fibres have no adsorptive power for common salt.

*Properties of the Paper made in Expts. 4 to 8.*—Handle and rattle: Better than in the unsized paper.

Colour: White, as the original material.

The strength should be greater in *Expt. 7* than in *Expt. 3*, owing to the increased amount of silicic acid in the paper (89% against 72%).

The use of salt for precipitating silicic acid from silicate solutions is out of the question in practice, owing to the uneconomical nature of the process. The amounts of salt used (150% of the weight of the pulp) are out of proportion to the increased fixation of silicic acid in the paper, and, in addition, it is impossible to use the wash water again on the paper machine with such a method of working.

**SIZING WITH THE MONOSILICATE OF METASILICIC ACID.**—A series of experiments was carried out with the monosilicate to correspond with the earlier experiments with the trisilicate. The same amounts of  $\text{SiO}_2$  were used.

*Expt. 11 (compare Expt. 1).*—36.2% monosilicate of 11° Bé. = 1.28%  $\text{SiO}_2$ .

Two litres of pulp, containing 50 gm. of air-dried paper, were treated with 36.2 c.c. of monosilicate solution (1:2). After stirring for half an hour the mixture was treated with 35 c.c. of aluminium sulphate solution, stirred for another half-hour and then filtered, washed and sampled. The quantity of alum solution used for precipitation, calculated on the dry paper, amounts to 7.0%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

*Examination of the Wash Water :*

Used : 0.64 gm.  $\text{SiO}_2$ .

Found in wash water : 0.26 gm.  $\text{SiO}_2$ .

Therefore 41% of the  $\text{SiO}_2$  remains in the water, and 59% in the pulp.

Calculated on an air-dried fibre, the silicic acid taken up amounts to 0.76%.

*Expt. 12 (compare Expt. 3).—*104.3% monosilicate of  $11^\circ \text{Bé.} = 7.40\% \text{SiO}_2$ .

Method as above. 160 c.c. of alum solution (i.e., 32%  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) was used for precipitation.

*Examination of the Wash Water :*

Used : 3.70 gm.  $\text{SiO}_2$ .

Found in wash water : 3.08 gm.  $\text{SiO}_2$ .

Thus 83% of the  $\text{SiO}_2$  remains in the milky wash water, and only 17% (or 1.23% on the dry pulp) in the paper.

*Properties of the Paper.*—Strength : Breaking length, 4,400 m. against 4,300 m. for the unsized paper. The stretch is diminished by 0.4% to 3.20%.

Handle and rattle : Better than the unsized paper.

Colour : White as the original sample.

Capillary rise in one hour at  $20^\circ \text{C.}$  :

Water : Mean 31 mm.

Printing varnish : 7.2 mm.

. The use of the monosilicate for sizing instead of the trisilicate is not to be recommended. Apart from the fact that less silicic acid is left in the pulp, the strongly alkaline monosilicate requires a much greater quantity of aluminium sulphate, which is largely wasted as sodium sulphate. Since, in addition, the price of the monosilicate is higher, its use is uneconomical.

The samples from Expts. 11 to 13 were somewhat whiter than the original paper, and the surface quality, together with better handle and rattle of the paper substance, is more silky than that of papers sized with polysilicate. This pro-

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perty of the paper sized with monosilicate may be due to a swelling of the fibres in the solution, which, before the precipitation, is three times as alkaline as in the polysilicate sizing.

**PRECIPITATION OF SILICIC ACID WITH MAGNESIUM SULPHATE.**—Under the title "Is Mineral Sizing of Printing Paper with Magnesium Sulphate and Silicate Possible?" (*W. f. P.*, 1913, vol. 45, p. 4251), Arno Froberg publishes a series of experiments on the precipitation of silicate solutions with magnesium sulphate and with a mixture of magnesium and aluminium sulphates, without, however, extending the experiments to actual paper-making trials.

The dilution of the solutions and the amounts of monosilicate used correspond to a 2% sizing of a pulp of 10% density. The precipitations were carried out in 500 c.c. of liquid, corresponding, for 10% pulp density, to 50 gm. of air-dried paper.

It seemed important to carry out these experiments in the presence of fibre in such a way as to be comparable with the earlier experiments, that is to say, with a pulp density of 2.5%.

As a preliminary experiment on the practical use of magnesium sulphate it was necessary to determine whether decomposition of the magnesium sulphate and absorption of magnesium hydroxide by the fibre occurs, as in the case of aluminium sulphate.\*

Recent researches after the carrying out of this investigation have made it appear probable that we are dealing with a chemical action of the inorganic and organic impurities in the commercial pulps upon the aluminium sulphate, and in the case of hemi-cellulose hydrates, that the colloidal cellulose itself can bring about the decomposition of the aluminium sulphate, which reaches a fairly high value.† ‡

\* Schwalbe and Robsahm, *W. Be.*, 1912, p. 1454.

† Lew, *Papier Fabrikant*, 1914, Nos. 34, 35, 36, 37; Heuser, *Papier Fabrikant*, 1914, pp. 1190, 1205.

‡ Schwalbe and Becker, *Zeitschr. für angew. Chem.*, 1919, pp. 265, 355; see also Heuser, "Lehrbuch der Cellulosechemie Bornträger," Berlin, 1921, p. 123.

40 gm. of "Ia. bleached Mitscherlich cellulose" were treated with 100 c.c. of 10% magnesium sulphate solution and stirred for an hour. The concentration of cellulose was 2.5%; the magnesium sulphate solution contained 10 gm.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in 100 c.c. After stirring, the mixture was filtered and washed until the total filtrate amounted to 2,000 c.c.

The  $\text{SO}_3$  in 100 c.c. of wash water was then estimated gravimetrically.

Used : 100 c.c. of water.

Found : 0.4811 gm.  $\text{BaSO}_4$ .

The total filtrate therefore contains 9.6220 gm.  $\text{BaSO}_4$ , corresponding to 3.9600 gm.  $\text{SO}_4$ , instead of 3.8974 gm. calculated. The small increase may be ascribed to solution of  $\text{CaSO}_4$  from the cellulose fibre.

The  $\text{SO}_4$  is, therefore, recovered completely in the wash water.

The magnesium was determined gravimetrically as magnesium pyrophosphate.

Used : 100 c.c. wash water.

Found : 0.2340 gm.  $\text{Mg}_2\text{P}_2\text{O}_7 = 0.0511$  gm. Mg.

The total wash water therefore contains 1.0220 gm. Mg., instead of 1.00 according to theory.

The wash water therefore contains all the  $\text{SO}_4$  and all the magnesium, and, at the temperature of the experiment, no decomposition or adsorption of the magnesium sulphate is caused by the cellulose or by the impurities contained in it.

Frohberg used for his precipitations the commercial trisilicate of metasilicic acid, to which he added sufficient caustic soda to reduce the ratio of  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  to that corresponding to monosilicate. Magnesium sulphate was added in equivalent proportions.

*Expt. 13.*—The proportions were the same as in Frohberg's second experiment (*W. f. P.*, 1914, p. 426). Accordingly, the following quantities were used :—

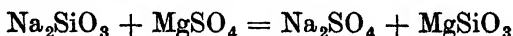
0.500 gm.  $\text{SiO}_2$ , corresponding to 1.91 gm. of  $38^\circ$  Bé.

s.s.

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silicate. This quantity contained 0.151 gm.  $\text{Na}_2\text{O}$ . To give a ratio  $\text{Na}_2\text{O} : \text{SiO}_2 = 62.00 : 60.30$ , 0.514 gm. of  $\text{Na}_2\text{O}$  to 0.500 gm.  $\text{SiO}_2$  are required. Therefore  $0.514 - 0.151 = 0.363$  gm.  $\text{Na}_2\text{O}$  must be added in the form of  $\text{NaOH}$ . An approximately 10% solution, containing, according to titration, 0.096 gm.  $\text{Na}_2\text{O}$  per c.c., was used. 0.363 gm.  $\text{Na}_2\text{O}$  therefore corresponds to 3.8 c.c., and this amount of the 10% solution was added to the 1.91 gm. of water glass.

According to the reaction :



60.30 gm.  $\text{SiO}_2$  require 40.32 gm.  $\text{MgO}$ , or 9.500 gm.  $\text{SiO}_2$  requires 0.337 gm.  $\text{MgO}$ .

0.337 gm.  $\text{MgO}$  corresponds to 2.06 gm. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and this quantity of magnesium sulphate contains 0.669 gm.  $\text{SO}_3$ .

To 2 litres of pulp, containing 50 gm. of fibre, was therefore added a mixture of 19.10 c.c. silicate solution (1 : 10) = 1.91 gm. of 38° Bé. silicate and 0.363 gm.  $\text{Na}_2\text{O}$  in the form of caustic soda solution. The mixture was stirred for half an hour and then treated with 20.6 c.c. of 10% magnesium sulphate solution = 0.337 gm.  $\text{MgO}$ . Stirring was continued for a further half-hour.

The mixture was then filtered as completely as possible, but not washed, since this experiment is intended to be parallel to those in which precipitation took place in the absence of fibre.

The filtrate amounted to 1,855 c.c. Including the water remaining in the fibre, the total water amounted to 2,235 c.c. It was milky in appearance.

The pulp showed an alkaline reaction. Even at a dilution of 1 : 1,000 the liquid still reacted alkaline.

The wash water was analysed for  $\text{SiO}_2$  and  $\text{MgO}$  by the usual methods.

(1)  $\text{SiO}_2$  determination :

Used : 0.500 gm.  $\text{SiO}_2$ .

Found in wash water : 0.3717 gm.  $\text{SiO}_2$ , that is, 74% in the water and 26% in the fibre.



Calculated on the air-dried pulp, this amounts to an absorption of 0.26%  $\text{SiO}_2$ .

(2)  $\text{MgO}$  determination :

Used : 0.337 gm.  $\text{MgO}$ .

Found : 0.8654 gm.  $\text{Mg}_2\text{P}_2\text{O}_7 = 0.313$  gm.  $\text{MgO}$ .

Therefore 93% of the magnesium sulphate passes into the wash water and 7% into the fibre.

Calculated on the air-dried pulp, the absorption of  $\text{MgO}$  amounts to 0.05%.

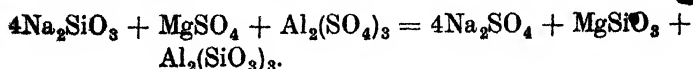
This experiment shows that only 26% of the silicic acid remains in the fibre and only 7% of the magnesium sulphate. In the precipitation without fibre 97.2% of the silicic acid and 65.6% of the magnesium sulphate remained in the precipitate.

The precipitation of  $\text{SiO}_2$  was thus in this case only 27% of the precipitation without fibre, while the magnesia precipitation only reached 11% of its former value. In this case, too, the fibre was not washed, as it has to be in order to imitate the conditions of the papermaking machine.

Accordingly the precipitation of silicate with magnesium sulphate alone is not to be recommended, since, in addition to the small absorption of  $\text{SiO}_2$  and  $\text{MgO}$ , the alkaline reaction is disadvantageous.

**PRECIPITATION OF SILICIC ACID FROM SILICATE SOLUTIONS WITH MAGNESIUM AND ALUMINIUM SULPHATES.**—In the above-mentioned work of Froberg, further experiments on the precipitation of silicic acid with aluminium sulphate and magnesium sulphate in the absence of fibre are described. The commercial trisilicate of metasilicic acid was again brought to the  $\text{Na}_2\text{O} : \text{SiO}_2$  ratio of the monosilicate by addition of caustic soda.

The reaction follows the equation



In the precipitation without fibre, as in Expt. 13 above, as much magnesium sulphate was added to the monosilicate

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solution as corresponded to complete reaction with  $\text{Na}_2\text{SiO}_3$ . In addition, aluminium sulphate corresponding to 0.067 gm.  $\text{Al}_2\text{O}_3$  was added.

If  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  participate in the reaction with  $4\text{Na}_2\text{SiO}_3$  (corresponding to 0.500 gm.  $\text{SiO}_2$ ) in the proportions indicated by the above equation, then 0.2495 gm.  $\text{MgSO}_4$  (= 0.0836 gm.  $\text{MgO}$ ) and 0.710 gm.  $\text{Al}_2(\text{SO}_4)_3$  (= 0.2118 gm.  $\text{Al}_2\text{O}_3$ ) must be used.

In this case, it is desired to perform in presence of fibre an experiment parallel to that carried out by Froberg in the absence of fibre. The quantities were therefore chosen as in Expt. 13, with the addition of aluminium sulphate corresponding to 0.067 gm.  $\text{Al}_2\text{O}_3$ . Froberg, after finding that the precipitate at first reacted acid, and later alkaline, in a succeeding experiment, allowed it to stand for five hours in order to obtain equilibrium before examining the filtrate.

*Expt. 14.*—To 2 litres of pulp, containing 50 gm. of fibre, the following solutions were added: 19.1 c.c. silicate solution (1 : 10) = 0.500 gm.  $\text{SiO}_2$ ; 3.8 c.c. approximately 10% caustic soda = 0.363 gm.  $\text{Na}_2\text{O}$ . After stirring for half an hour, 20.6 c.c. of 10% magnesium sulphate solution (= 0.337 gm.  $\text{MgO}$ ) and 4 c.c. of 10% aluminium sulphate solution (= 0.067 gm.  $\text{Al}_2\text{O}_3$ ). The mixture was then stirred for a further half-hour, after which it was allowed to stand for thirteen and a half hours, stirred again for one hour and then filtered, but not washed.

#### *Examination of Wash Water :*

Volume of filtrate	1,875 c.c.
Weight of wet pulp	427 gm.
Combined weight of pulp and liquor	2,302 gm.
Air-dried pulp	50 gm.
Volume of filtrate	2,252 c.c.

The total water thus amounted to 2,252 c.c. It was very milky and gave an alkaline reaction.

A silica determination gave 0.3559 gm.  $\text{SiO}_2$ .

The original amount used was 0.500 gm., and therefore 71% of the  $\text{SiO}_2$  is recovered from the wash water and 29% remains in the pulp. Calculated on the air-dried pulp, the amount of  $\text{SiO}_2$  taken up is 0.28%.

In a magnesium estimation 0.7169 gm.  $\text{Mg}_2\text{P}_2\text{O}_7 = 0.2596$  gm.  $\text{MgO}$  was obtained.

The amount of  $\text{MgO}$  originally added was 0.337 gm. and 77% of the  $\text{MgO}$  passes into the water and 23% remains in the pulp.

Calculated on the air-dried pulp, this amounts to an absorption of 0.16%  $\text{MgO}$ .

In this experiment it is seen that only 29% of the  $\text{SiO}_2$  and 23% of the  $\text{MgO}$  remained in the pulp, while in the experiments without fibre 97%  $\text{SiO}_2$  and 93%  $\text{MgO}$  were precipitated.

Although the pulp was not washed, the precipitation of  $\text{SiO}_2$  was therefore only 29.6% of that obtained without fibre, while the precipitation of  $\text{MgO}$  was only 25% of that formerly found. In addition, the mixture was still alkaline, which is disadvantageous in practice.

In order specially to remove this latter difficulty, an experiment was carried out in which sufficient alum solution was added to allow it to react with the whole of the sodium silicate, and leave the pulp slightly acid.

*Expt. 15.*—Two litres of pulp, containing 50 gm. of air-dried fibre, required 13 c.c. of alum solution to produce a slightly acid reaction.

The experiment was carried out as before.

Monosilicate corresponding to 0.500 gm.  $\text{SiO}_2$  was added, the mixture was stirred for half an hour and precipitated with magnesium sulphate solution containing 0.337 gm.  $\text{MgO}$  and with 25.6 c.c. of alum solution. The reaction was then faintly acid. After stirring for a further half-hour the mixture was filtered. The filtrate was clear.

As previously determined, 13 c.c. of the 25.6 c.c. of alum solution were used in neutralising the pulp, so that 12.6 c.c.

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containing 0.2112 gm.  $\text{Al}_2\text{O}_3$  were available for precipitation of the silicic acid.

*Examination of Filtrate.*—Of the 0.500 gm  $\text{SiO}_2$  originally added 0.1495 gm.  $\text{SiO}_2$  was found in the filtrate (2,323 cm. total volume). Therefore 30% of the  $\text{SiO}_2$  passed into the filtrate and 70% into the pulp.

Calculated on an air-dried pulp the absorption of  $\text{SiO}_2$  amounts to 0.70%.

0.9308 gm.  $\text{Mg}_2\text{P}_2\text{O}_7 = 0.337$  gm.  $\text{MgO}$ , the total amount used, was found in the filtrate.

This experiment shows, therefore, that the silicic acid reacts with the aluminium sulphate alone, while magnesium sulphate passes into the filtrate without decomposition.

70% of the  $\text{SiO}_2$  remained in the pulp, while Froberg found 95.6% in his precipitate. The amount of  $\text{SiO}_2$  precipitated in the present experiment is therefore only 73% of that obtained by Froberg.

*Properties of the Paper.*—Strength : The breaking length was 4,550 m. or 250 m. higher than that of the original material. The stretch was reduced by 0.2%.

Handle and rattle : Better than in the original material.

Colour : White, as that of the original.

Capillary rise in one hour at  $20^\circ \text{C}$ . :

Water : Mean 31 mm.

Printing varnish : Mean 7 mm.

*Expt. 16.*—This experiment was carried out with the same amounts of  $\text{Na}_2\text{SiO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{MgSO}_4$  as before, but after the addition of the silicate 10 gm. of china clay in the form of paste were added. The mixture was washed until the total filtrate amounted to 6 litres. It was slightly cloudy owing to suspended particles of china clay.

*Estimation of Loading Material.*—An ash determination on paper from Expt. 15 gave 1.59% ash.

An ash determination on the sized and loaded paper gave 13.40% ash.

Of this 13.40% ash,  $(13.40 - 1.59) = 11.81\%$  consisted of

ignited china clay, or  $11.81 + 1.60$  (allowing 13.50% for loss of weight on heating) = 13.41% actual china clay.

The paper thus contained 13.41% of china clay, or 67% of the amount originally added.

This fixation of filling material is thus about 20% higher, on the total amount used, than with the loaded but unsized paper (47% fixation, see Expt. 3c', p. 19), and about 17% higher than with the paper treated with  $\text{Al}_2(\text{SO}_4)_3$  and loaded (50% yield, see Expt. 3c'', p. 20).

The results of the foregoing experiments should answer the question in the title of Froberg's paper, "Is Mineral Sizing of Printing Paper with Magnesium Sulphate and Silicate possible?" in the negative, at least from a technical point of view. When magnesium sulphate alone is used for the precipitation, it is seen that, in addition to the low fixation of silicic acid (26%  $\text{SiO}_2$ ), an alkaline reaction in the pulp is obtained which is fatal to aniline colours and to efficient use of fibre and loading material. If, on the other hand, alum is added in sufficient quantity to produce a faint acid reaction, the same amount is needed as when no magnesium sulphate is present, the latter remaining entirely in the wash water.

Froberg actually comes to the same conclusion, although experiments performed in the absence of fibre, and without regard to the conditions obtaining in practice, are not sufficient for answering such a question as the above.

**SIZING OF "NEWS" WITH SILICATE.**—In the preceding experiments only bleached cellulose fibre was used. The cheapness of silicate sizing makes it particularly suitable for use with cheaper papers containing mechanical pulp. Experiments on the sizing of "news" were, therefore, carried out on a furnish containing 80% mechanical pulp and 20% cellulose.

*Expt. 17.*—30% of 38° Bé. silicate.

To 2 litres of pulp containing 40 gm. of wood pulp (Weiss-schliff) and 10 gm. of bleached Mitscherlich cellulose 15 gm. of 38° Bé. silicate solution were added. After half an hour's

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stirring the mixture was precipitated with 85 c.c. of 10% alum solution ( $= 17\% \text{ Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  calculated on the air-dried fibre) until a faintly acid reaction was obtained. Stirring was then continued for half an hour, after which the mixture was filtered, washed until the filtrate amounted to 6 litres, and sampled.

*Properties of the Paper.*—Strength: The breaking length was 3,200 m., or 500 m. and 350 m. higher than for paper unsized and treated with alum solution respectively (see Expts. 18 and 19).

The stretch was unaltered, 1.89%.

Handle and rattle: Distinctly better than with the flabby unsized paper.

Colour: Brighter than that of the original material.

Capillary rise in one hour at  $20^\circ \text{C}$ .:

Water: Mean 40 mm.

Printing varnish: Mean 8 mm.

*Expt. 18.*—In order to compare the properties of sized and unsized paper, a sample was treated with aluminium sulphate alone, as is usual in practice. 2% of crystallised  $\text{Al}_2(\text{SO}_4)_3$  was used.

*Properties of the Paper.*—Strength: Breaking length, 2,853 m. Stretch, 1.76%.

Handle and rattle: Poor.

Colour: As in original material.

In order to determine the retention of loading, the material was incinerated.

An ash determination gave 1.20% ash.

*Expt. 19.*—Two litres of pulp containing 40 gm. of "Weiss-schliff" and 10 gm. cellulose were sampled after one hour's stirring.

*Properties of the Paper.*—Strength: Breaking length, 2,708 m. Stretch, 1.80%.

Handle and rattle: Poor.

Most papers containing wood pulp are loaded, and a determination was therefore made of the amount of filler

taken up by the fibre, and also of the alteration of the strength by loading. In this case another wood pulp (Muldenstein) was used, and only 15% of 38° Bé. silicate.

*Expt. 20.*—15% of 38° Bé. silicate.

The method was as in the previous experiment, but 7.5 gm. of 38° Bé. silicate (= 15% on the dried pulp) were used.

*Properties of the Paper.*—Strength: Breaking length, 3,340 m. Stretch, 1.45%.

Handle and rattle: Very good.

Colour: Brighter than that of the original material.

Capillary rise in one hour at 20° C.:

Water: Mean 26 mm.

Printing varnish: Mean 7 mm.

In order to determine the filling material in the following experiment it was necessary to estimate the ash in this sized but unloaded paper. This was found to be 4.95%.

*Expt. 21.*—15% of 38° Bé. silicate and 20% china clay.

7.5 gm. of 38° Bé. silicate and 10 gm. of china clay "pulp" added to 2 litres of pulp containing 40 gm. of "Weiss-schliff" and 10 gm. of cellulose. The mixture was stirred for half an hour, and then treated with alum solution until slightly acid. The filtrate was only slightly turbid, owing to suspended particles of china clay.

*Estimation of Filling Material.*—The ash content was found to be 20.72%.

This 20.72% of ash contained  $(20.72 - 4.95) \% = 15.77\%$  of ignited china clay. Allowing for 2.13% loss on heating, this corresponds to 17.90% of actual china clay.

The paper therefore contains 17.90% of china clay, or 90% of the amount added.

To determine the influence of silicate precipitation on the retention of loading in the paper, the following sample was prepared:—

*Expt. 22.*—20% china clay with  $\text{Al}_2(\text{SO}_4)_3$ .

Two litres of pulp containing 40 gm. of "Weiss-schliff"

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and 10 gm. bleached cellulose were stirred for half an hour with 10 gm. of china clay paste and treated with alum solution until acid, being then filtered and washed. Samples were taken, as usual, at a dilution of 1 in 1,000.

The ash content of the sample was 16%.

In order to calculate the actual amount of loading corresponding to the 16% of ash, 1.20% must be subtracted for the ash of the paper treated only with alum and not loaded (*Expt. 18*).

In the above 16% of ash there is therefore  $(16 - 1.20)\% = 14.80\%$  of ignited china clay, or  $(14.80 + 2) = 16.80\%$  of actual china clay. This corresponds to 84% of the amount added.

Here again, therefore, there is an increase in the fixation of filling material of 6%, when silicate is used, compared with printing paper treated with aluminium sulphate alone.

*Strength and Quality of the Paper.*—Strength: The breaking length of the sized and loaded paper was 2,825 m., 175 m. more than that of the loaded paper treated with alum solution (2,654 m.). Stretch 1.50%, unaltered.

Handle and rattle: Better than with the loaded and alum-treated paper, which was flabby.

Colour: Brighter than that of the original material.

Capillary rise in one hour at 20° C.:

Water: Mean 25 mm.

Printing varnish: Mean 7 mm.

**SUMMARY OF THE RESULTS OF PURE MINERAL SIZING.**—An examination of the results recorded in the preceding pages will show that in all the experiments with silicate (in particular the trisilicate is meant) an increase in breaking length ranging from 8.2% in the case of newspaper to 18.5%, compared with the unsized raw material, is obtained. The increase in loading amounts to 30% of the filler in unsized (loaded) paper, while the breaking lengths of these silicate-sized and loaded papers do not fall below the values for the unsized and unloaded raw material.



Further, in the case of all silicate-sized papers there is an increased capillary rise both for aqueous solutions and for printing varnish. This is of importance in practice, since with quick printing a sharper, more "plastic," and more permanent impression is obtained.

## CHAPTER II

### SILICATE AND ROSIN SIZING

SIZING BY THE METHOD OF D.R.P. No. 245,975, OF KULDKEPP AND GRAF.—It is an obvious step to utilise the alkaline properties of silicate solution for the complete or partial saponification of rosin, in order to obtain a precipitate of “resin-aluminium silicate,” by the treatment of such a solution with aluminium sulphate.

Two patents have already been mentioned in the Introduction whose object is the use of silicate in conjunction with rosin as a sizing material. The first of the two methods is that of A. Kuldkepp and Graf, No. 245,975. The claim reads as follows :—

“A method for the preparation of a resin soap for paper sizing by the use of sodium silicate in which the rosin, casein, or similar compound is intimately mixed with the silicate at a temperature so low that silicic acid is not liberated.” \*

As an example, a size was described in which 8.2 parts of rosin powder were mixed with 2 parts of water, 3 parts of 30° Bé. soda solution, and 6.8 parts of 41° Bé. silicate at room temperature, the mixture being subsequently dissolved in water at 70° C.

In accordance with these instructions 8.2 gm. of rosin powder were well mixed with 3 gm. of 30° Bé. soda solution and 7.3 gm. of 38° Bé. silicate (equivalent to 6.8 parts of 41° Bé. solution), dissolved in water at 70°, and made up to 1,000 c.c.

A large quantity of silicic acid was precipitated in the form of a fine powder, and the liquid after settling was of a clear light-brown colour.

\* *V. Bl.*, 1912, p. 1549.

A second preparation was then made with the same proportion, but using 2 litres of water at 30° to 35° C. In this case also a large amount of silicic acid separated, and the solution had a milky appearance.

This second experiment shows that the temperature has no effect on the precipitation of silicic acid. To confirm this observation solutions of silicate at dilutions of 1 : 10, 1 : 5, 1 : 2, and also undiluted 38° Bé. solution, were warmed to 80° C without the precipitation of any trace of silicic acid. The condition as to temperature in the patent specification is therefore valueless.

In order to discover the reason of the separation of silicic acid in size made by the above method, the ratio of rosin to alkali was calculated. 3 gm. of 30° Bé. soda solution were added to 8.2 gm. of rosin powder. 100 gm. of 30° Bé. soda solution contain 24.18 gm.  $\text{Na}_2\text{CO}_3$ , and the amount of soda added was therefore 0.725 gm., or 8.8464 gm. per 100 gm. of rosin.

The soda figure for the American rosin used was found by analysis to be 15.662 gm.  $\text{Na}_2\text{CO}_3$  per 100 gm. In the experiment therefore  $(15.6620 - 8.8464) = 6.8156$  gm. more soda were required for saponification per 100 gm. rosin, or 0.5589 gm. anhydrous soda on 8.2 gm. rosin.

This deficit of 0.5589 gm.  $\text{Na}_2\text{CO}_3$  ( $= 0.3269$  gm.  $\text{Na}_2\text{O}$ ) was made up at the expense of the 7.3 gm. of 38° Bé. silicate originally added. According to analyses already given, the alkalinity of the silicate obtained from v. Baerle & Co. amounts to 7.912%  $\text{Na}_2\text{O}$ . 7.3 gm. therefore contains 0.5776 gm.  $\text{Na}_2\text{O}$ .

Since only 0.3269 gm.  $\text{Na}_2\text{O}$  is required to complete the saponification, the excess is  $(0.5776 - 0.3269) = 0.2507$  gm.  $\text{Na}_2\text{O}$ .

The size given in the patentee's example was therefore "fully saponified," and, taking into account the total alkali of the silicate, contained an excess of alkali.

In order to estimate the amount of silicic acid precipitation during the solution of the first size preparation, the

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silica content of the resulting solution was determined, as follows:—

100 c.c. portions of the clear settled size solution were precipitated with hydrochloric acid in a filter funnel. The resin acid was extracted with ether and the aqueous solution removed. The ethereal solution was then shaken several times with dilute hydrochloric acid, and the silicic acid determined on the whole of the aqueous portion.

In 100 c.c. of size solution there was found 0.0204 gm.  $\text{SiO}_2$ . 1,000 c.c. of the solution therefore contain 0.2040 gm.  $\text{SiO}_2$ . 7.3 gm. of 38° Bé. silicate were originally used, corresponding to 1.9126 gm.  $\text{SiO}_2$ . Therefore 10.67% of the  $\text{SiO}_2$  remains in the solution, the remaining 89.23% being precipitated.

The precipitation of this large quantity of silicic acid during the preparation of the size is a source of considerable loss, besides which the fine precipitate will collect in the size containers, necessitating frequent cleaning. If the silicic acid is maintained in suspension by stirring, there is danger of stopping up the wire of the paper machine.

In order to dispose of the suggestion that the size was not properly prepared, a piece of resin soap as prepared by a licensee of the patent was obtained and dissolved; it gave the same heavy precipitate of silica as before. This is in direct contradiction to the statements in the Patent Specification, which mentions this silica precipitation as one of the disadvantages of known methods of saponifying rosin with silicate in warm solution, and claims to have avoided it by the new process.

Before any sizing experiments were carried out it was necessary to discover the cause of the precipitation.

The most likely cause for the separation of silica was the removal of alkali from the trisilicate; another possibility was the formation of small quantities of carbon dioxide by dissolving the soda soap in warm solution. The following experiment was therefore carried out:—

(a) Rosin powder and silicate were mixed together in such proportions that the total alkalinity of the silicate

was just sufficient for saponification of the rosin. 100 gm. of American rosin required, by experiment, 15.6620 gm.  $\text{Na}_2\text{CO}_3$ ; i.e., 10 gm. of rosin require 1.5662 gm.  $\text{Na}_2\text{CO}_3$ , or 0.9161 gm.  $\text{Na}_2\text{O}$  for complete saponification.

The total alkalinity of the 38° Bé. silicate was 7.912%, and therefore 11.58 gm. silicate are required to supply the alkali for complete saponification of the rosin.

10 gm. of rosin powder were therefore mixed with 11.58 gm. of 38° Bé. silicate in a mortar in the cold. The whole of the mixture was then dissolved in water at 80° and made up to 1,000 c.c. A heavy precipitate of silicic acid was formed, while the clear liquid above the precipitate was light brown.

The silicic acid in this preparation was then estimated, as follows:—

50 c.c. portions of the clear settled solution were analysed for silicic acid by the usual method. By repeated evaporation to dryness only a brown ring could be seen in the crucible. After moistening with hydrochloric acid and heating with water, a clear yellow solution was obtained without any solid. There was, therefore, no silicic acid left in the solution, all having been precipitated.

(b) Rosin powder and silicate were mixed together in such proportions that five times as much silicate was present as sufficed for complete saponification of the rosin.

10 gm. of rosin powder were mixed with 28.95 gm. of 38° Bé. silicate in a mortar until the mass crumbled away from the walls of the vessel. The whole was now dissolved in water at 75° to 80° C. and made up to 1,000 c.c. A small amount of  $\text{SiO}_2$  separated, but the solution itself was clear and dark and brown.

These two experiments show that the cause of silica separation is the removal of alkali from the silicate. On complete removal of alkali, the silicic acid is quantitatively precipitated, while on removal of smaller amounts of alkali a smaller amount of silica is precipitated. The fact that in the second case less alkali is removed from the water glass is explained by the free alkali content of the silicate.

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solution. Thus in the second case, owing to the fourfold excess of silicate, a smaller amount of alkali was removed by saponification of the rosin. This explains the fact that by further increase in the amount of water glass the precipitation of silicic acid can be reduced. When the saponification is once completed an excess of silicate remains unaltered, as the following experiment shows.

(c) 5 gm. of rosin in the form of a brown, completely saponified resin soap, were mixed in a mortar with 50 gm. of 38° Bé. silicate to a homogeneous, viscous mass, and then dissolved in water at 80° and diluted to 1,000 c.c. The light-brown, clear size showed no trace of precipitated silicic acid.

It may be remarked that the size solution was originally made up to a total volume of 500 c.c.; in these circumstances it was milky when cool. In order to obtain a clear solution it was necessary to dilute to 1,000 c.c.

In order to study the influence on the silicate of the carbon dioxide formed by solution of sodium soap, the following experiments were carried out:—

(d) 5 gm. of finely powdered rosin were mixed in a mortar with 4 gm. of a 20% soda solution (sufficient for complete saponification) and 50 gm. of 38° Bé. silicate to a homogeneous viscous liquid. The soap was then dissolved in water at 80°. When the total volume was made up to 500 c.c. the solution became milky on cooling, and it was therefore diluted to 1,000 c.c. with warm water. A slight deposit of silicic acid was visible in the clear brown solution. This was thought to be due to evolution of carbon dioxide from the cold soda soap.

A further proof is given by the following experiment (compare (c)):—

(e) 5 gm. of rosin powder were mixed in the cold with 6 gm. of a 10% caustic soda solution (sufficient for complete saponification) and stirred with 50 gm. of 38° Bé. silicate to a homogeneous mass. The mixture was dissolved in water at 80°. Since dilution to 500 c.c. gave a milky solution,

the total volume was made up to 1,000 c.c. No trace of silicic acid was deposited.

The above results show that, in the method used by Kuldkepp and Graf for preparing size, part of the deposit of silicic acid is due to the liberation of carbon dioxide.

As mentioned above, silicic acid which is precipitated in the liquid size solution is lost for practical purposes, and it is therefore unlikely that the size prepared by the above method would be adopted. The claims made for the process \* that it finally solves the thirty-year-old problem of rosin sizing hardly seems justified.

The small mixer used for the intimate mixing of the silicate and rosin, said to increase the "sizing efficiency" of the product, can obviously not alter the saponification number of the rosin or affect the chemical reaction between silicate and rosin. It can hardly be imagined that the author intended the grinding to give the solid rosin so large a specific surface as to make the solution approach the colloidal condition.

Experiments were next made on sizing with rosin-silicate size.

*Expt. 23.*—Kuldkepp and Graf's size containing 1.64% of resin.

Two litres of pulp containing 50 gm. of dry "Ia bleached Mitscherlich cellulose" were treated with 100 c.c. of size solution (= 0.82 gm. resin) made according to the first example of Kuldkepp and Graf, the mixture stirred for half an hour, after which 26 c.c. 10% alum solution were added, giving an acid reaction; this corresponds to 5.2%  $\text{Al}_2(\text{SO}_4)_3$ . Aq. on the dry cellulose. After further stirring for half an hour the mixture was filtered, washed till the volume of liquid was 6 litres, and sampled at a dilution of 1 : 1000.

*Properties of the Paper.*—Handle and rattle: Fairly good in view of the amount of rosin used.

Colour: Whiter than that of a paper sized with rosin alone.

\* *W. Bl. f. P.*, 1912, p. 2230.

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Ease of writing (resistance to ink): Standard ink does not run or show through the paper.

Capillary rise in one hour at 20° C. :

Water : Mean 0.0 mm.

Printing varnish : Mean 7.5 mm.

*Expt. 24.*—Kuldkepp and Graf's size containing  $\frac{1}{2}\%$  of rosin.

To 2 litres of pulp (= 50 gm. air-dried fibre) 30.5 c.c. of size solution (= 0.25 gm. resin) were added. The mixture was stirred for half an hour, precipitated with 24 c.c. of alum solution to give an acid reaction; this amount of alum is equivalent to 4.8%  $\text{Al}_2(\text{SO}_4)_3$ . Aq. calculated on the air-dried pulp. The mixture was again stirred for half an hour, and afterwards filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle : Good for  $\frac{1}{2}\%$  rosin sizing.

Colour : Whiter than with  $\frac{1}{2}\%$  rosin alone (as in following experiment).

Resistance to ink : Standard ink runs slightly and shows through. The paper was worse in this respect than in the following experiment, carried out for the sake of comparison with rosin size alone.

Capillary rise in one hour at 20° C. :

Water : Mean 4 mm.

Printing varnish : Mean 9 mm.

For comparison, rosin sizing was carried out with ~~3%~~, 1%,  $\frac{1}{2}\%$  and  $\frac{1}{4}\%$  of rosin. The rosin was added to the pulp in the form of a "free" rosin suspension. With the mixture containing 3% of rosin a loaded paper was prepared, and the absorption of filler determined.

*Expt. 25A.*—3% rosin as a free rosin suspension.

70 c.c. of free rosin emulsion containing 1.5 gm. rosin were added to 2 litres of pulp, stirred for half an hour, and then treated with 15 c.c. of aluminium sulphate solution until the reaction was faintly acid. The amount of aluminium sulphate added corresponds to 3%  $\text{Al}_2(\text{SO}_4)_3$ . Aq. on



the air-dried pulp. The mixture was stirred for a further half hour, filtered, washed and sampled as before.

*Properties of the Paper.*—Strength: The breaking length was 3,990 m. as against 3,800 for the unsized paper—an increase of 190 m.

Handle and rattle: Good for 3% rosin sizing.

Colour: Slightly yellow in comparison with the original material.

Resistance to ink: Undoubtedly good.

Capillary rise in one hour at 20° C.:

Water: Mean 0.0 mm.

Printing varnish: Mean 7 mm.

An ash determination, made in order to enable the loading to be calculated, gave 0.80% ash.

*Expt. 25A.*—3% rosin and 20% china clay.

The method was the same as in 25A, but 10 gm. of china clay pulp were added to the pulp after the addition of the resin and before precipitation. The wash water was turbid owing to suspension of clay.

*Properties of the Paper.*—Strength: Breaking length, 3,100 m., i.e., 1,200 m. less than that of unsized and unloaded paper (4,300 m.). Stretch 3.31, or about 0.30% less than before.

Handle and rattle: Good.

Colour: Yellowish compared with original material.

Capillary rise in one hour at 20° C.:

Water: Mean 0.0 mm.

Printing varnish: Mean 7.5 mm.

The loading was determined by ignition of the paper.

The ash found was 11.78%. This contains  $(11.78 - 0.81) = 10.97\%$  of ignited china clay, or  $(10.97 + 1.48)\%$  of actual china clay after allowing for the loss on ignition.

The paper therefore contains 12.45% of china clay, or 62.25% of the amount added.

*Expt. 25B.*—1% rosin as a free rosin emulsion.

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12.5 c.c. of the emulsion, containing  $\frac{1}{2}$  gm. of rosin were added to 2 litres of pulp containing 50 gm. of air-dried fibre. The mixture was stirred for half an hour, precipitated with 24 c.c. of 10% aluminium sulphate solution to give an acid reaction, and then stirred for a further half hour before being filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle : Good.

Colour : Yellow compared with the white raw material.

Resistance to ink : Standard ink does not run or show through the paper.

Capillary rise in one hour at 20° C.

Water : Mean 0.0 mm.

Printing varnish : Mean 7.3 mm.

*Expt. 25C.*— $\frac{1}{2}$ % rosin as a free rosin emulsion.

Method as in the previous experiment, with the addition of only half the amount of rosin.

*Properties of the Paper.*—Strength : The breaking length, 3,990 m. is 180 m. higher than that of the unsized material. Stretch is almost unchanged, 3.44 %.

Handle and rattle : Good.

Colour : Slightly yellow compared with the white raw material.

Capillary rise in one hour at 20° C.

Water : Mean 0.0 mm.

Printing varnish : Mean 7 mm.

Resistance to ink : Standard ink did not run or show through the paper.

*Expt. 25D.*— $\frac{1}{4}$ % rosin as a free rosin emulsion.

Method as before, with a correspondingly smaller amount of emulsion.

*Properties of the Paper.*—Handle and rattle : Almost the same as with unsized paper.

Colour : Slightly yellow.

Resistance to ink : Poor. Standard ink shows through the paper and runs slightly.

Capillary rise in one hour at 20° C.

Water : Mean 0.0 mm.

Printing varnish : Mean 7.2 mm.

For the sake of completeness, sizing experiments were carried out with the rosin-silicate solutions which were prepared in order to explain the precipitation of silica in the size of Kuldkepp and Graf (p. 47). Solutions which had a sediment of silicic acid were not shaken before use, but only the clear brown liquor was used.

*Expt. 26.*—Size *a*. 1% rosin.

50 c.c. of size *a* were added to 2 litres of pulp (= 50 gm. of air-dried pulp). After stirring for half an hour the solution was precipitated with alum and stirred for a further half hour. 20 c.c. of 10% alum solution were required to give an acid reaction to the mixture.

The resulting paper was similar to that obtained with normal 1% rosin sizing.

*Expt. 27.*—Size *b*.  $\frac{1}{2}$ % rosin.

40 c.c. of the clear brown size solution were added to 2 litres of pulp (= 50 gm. of air-dried pulp). The mixture was stirred for half an hour and treated to give an acid reaction with 22 c.c. of alum solution (= 4.4% alum on the dry fibre). After a further half hour's stirring the pulp was filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle : Better than with plain  $\frac{1}{2}$ % rosin sizing.

Colour : As white as the original material, in contrast to the yellow colour produced by plain rosin sizing.

*Expt. 28.*—Size *c*.  $\frac{1}{2}$ % rosin.

The method was as above. 50 c.c. of the size solution were used, i.e.,  $\frac{1}{2}$ % of rosin with 5% of 38° Bé. silicate.

*Properties of the Paper.*—Handle and rattle : Better than for  $\frac{1}{2}$ % pure rosin sizing.

Colour : The original white of the raw material.

Resistance to ink : Ink does not run or show through.

*Expt. 29.*—Size *d*.  $\frac{1}{2}$ % rosin.

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This was carried out in the same manner. 50 c.c. of size solution were used, containing  $\frac{1}{2}\%$  of rosin with 50% of 38° Bé. silicate. The resulting paper was similar to that produced in Expt. 28.

*Expt. 30.*—Size *e.*  $\frac{1}{2}\%$  rosin.

50 c.c. of the clear brown size solution were added to 2 litres of pulp containing 50 gm. of air-dried fibre and stirred for half an hour. After precipitation with 25 c.c. of alum solution ( $= 5\%$  of  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Aq.}$  calculated on the air-dried material), stirring was continued for a further half hour, after which the mixture was filtered and washed until the total wash water amounted to five litres, and then sampled in the usual manner.

Used : 2.5 gm. 38° Bé. water glass  $= 0.6550$  gm.  $\text{SiO}_2$ .

A silica determination showed the wash water to contain 0.3722 gm.  $\text{SiO}_2$ . Thus 56.83% of the  $\text{SiO}_2$  passes into the wash water and 43% remains in the pulp.

The fixation is thus 0.57% of the weight of the air-dried paper.

In dealing with the causes of the separation of silica in the size of Kuldkepp and Graf it was shown, in the case of sizes *a* and *b*, that an increase in the amount of silicate used for saponifying the rosin effected a reduction in the amount of silica precipitated, in comparison with that which occurred on adding an amount of silicate equivalent to the alkali required for saponification.

Further, in the saponification of fats described later, too large an amount of water glass was used owing to a mistake in weighing, and no silica separated. These observations suggested the following experiments.

*Preparation of Size for Expt. 31.*—5 gm. of rosin powder ground with 87 gm. of 38° Bé. silicate in the cold, and the mixture dissolved in warm water at 80° and made up to 1,000 c.c. A slight separation of silica occurred. In this case fifteen times the amount of silicate necessary for saponification was used.

*Preparation of Size for Expt. 32.*—5 gm. of rosin powder ground in the cold with 116 gm. of 38° Bé. silicate, dissolved in water at 80° and made up to 1,000 c.c. No separation of silica occurred. The silicate used, 116 gm., corresponds to twenty times the amount (5.79 gm.) requisite for complete saponification of the rosin.

In another experiment, the rosin was used in the form of coarse grains, and was saponified with 38° Bé. silicate by warming to 80°. In this case also, no precipitation of silica occurred on dissolving the soap.

The silicate-resin soap prepared by grinding or kneading with cold water may be dissolved in cold water; in this case the operation of dissolving requires more time unless larger quantities of water are used. This condition is, however, fulfilled in the hollander, and the silicate-resin soap may therefore be added directly to the mixture in the hollander, where the penetration of the size solution into the mass of the fibre takes place, assisted by the large volume of water present, and by the dispersing action of the roll. Precipitation with alum solution can then be carried out as usual.\*

*Expt. 31.*—Size prepared as above.  $\frac{1}{2}\%$  of rosin used.

50 c.c. of size solution (*i.e.*,  $\frac{1}{2}\%$  rosin and 8.7% of 38° Bé. silicate) were added to 50 gm. of fibre in 2 litres of pulp and stirred for half an hour. Precipitation was carried out with 26 c.c. of 10% aluminium sulphate solution ( $= 5.2\% \text{ Al}_2(\text{SO}_4)_3 \cdot \text{Aq.}$ ) and stirring continued for half an hour. The mixture was filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle: Better than for  $\frac{1}{2}\%$  rosin sizing.

Colour: White, as in the original material.

Resistance to ink: Standard ink does not run or show through.

\* The preparation of silicate-resin size without separation of silica by the methods given above is protected by the author under D.R.P., No. 320,820.

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*Expt. 32.*—Size prepared as above. 1% of rosin used.

100 c.c. of size solution (*i.e.*, 1% rosin and 23.2% 38° Bé. silicate) were added to 50 gm. of fibre in 2 litres of pulp. After stirring for half an hour, 45 c.c. of 10% alum solution ( $= 9\% \text{Al}_2(\text{SO}_4)_3 \cdot \text{Aq.}$ ) was added, to give an acid reaction. After further stirring for half an hour; the pulp was filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle : Better than for 1% pure rosin sizing.

Colour : As white as that of the unsized paper.

Resistance to ink : Standard ink does not run or show through.

Capillary rise in one hour at 20° C.

Water : Mean 0.0 mm.

Printing varnish : Mean 7 mm.

*Expt. 32B.*—Size as above.  $\frac{1}{2}\%$  of rosin used.

The method was as before. Precipitation was carried out, to give an acid reaction, with 30 c.c. of 10% alum solution, corresponding to 6% aluminium sulphate on the dry fibre. After filtering, the pulp was washed until 5 to 6 litres of wash water were obtained. This was slightly cloudy.

A determination of silica in the wash water gave 1.0669 gm.  $\text{SiO}_2$ .

The amount originally added was 1.520 gm. Therefore, 70% of the  $\text{SiO}_2$  passes into the wash water, leaving 30% in the pulp; the silica absorption thus amounts to 0.91% on the air-dried material.

*Properties of the Paper.*—Strength : Breaking length, 3,800 mm., or 160 m. higher than that of unsized paper from the same raw material. The stretch had increased by 0.4%, *i.e.*, to 3.55%.

Handle and rattle : Better than with pure rosin sizing.

Colour : White, as for the raw material.

Resistance to ink : Standard ink did not run, and still did not show through.

Capillary rise in one hour at 20° C.

Water : Mean 5 mm.

Printing varnish : Mean 7 mm.

The ash on this paper was determined, in order to measure the loading, in the next experiment, and was found to be 2.82%.

*Expt. 32c.*—Size as above, corresponding to  $\frac{1}{2}$ % of rosin, with the addition of 20% of china clay.

The method was the same as in the previous experiment, but after the addition of the size 10 gm. of china clay as pulp were added. The amount added corresponded to 20% of the air-dried pulp.

*Properties of the Paper.*—Strength : The breaking length was 3,340 m., about 300 m. lower than that of unsized and unloaded paper. The diminution of 300 m. is however small in comparison with the 1,200 m. diminution for loaded paper sized with the ordinary 3% rosin size. The stretch, 3.13%, was almost unchanged.

Handle and rattle : Better than for paper loaded, but not sized.

Colour : As white as the original material.

Resistance to ink : Standard ink ran easily and showed through to some extent.

Capillary rise in one hour at 20° C.

Water : Mean : 11 mm.

Printing varnish : Mean 7 mm.

In order to estimate the absorption of china clay the paper was ignited and found to give 14.19% ash.

This 14.19% ash contains  $(14.19 - 2.82) = 11.37\%$  of ignited china clay, or 13.15% of actual china clay.

The paper thus contained 13.15% of china clay, or 64% of the amount added.

There is therefore an increased fixation of 4%, calculated on the amount of clay added, over that obtained with the expensive 3% rosin size : at the same time, the diminution

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of strength is only one-fourth of that produced in the latter case.

Corresponding with the size used in Expts. 32, some rosin powder was saponified with an amount of monosilicate containing twenty times the quantity of alkali requisite for complete reaction.

*Preparation of Size for Expt. 33.*—By experiment 1 gm. of rosin needed 1.158 gm.  $\text{Na}_2\text{O}$ . 100 gm. of monosilicate, according to analysis, contained 3.621 gm.  $\text{Na}_2\text{O}$ ; the amount of silicate needed for saponification is therefore 31.98 gm. Twenty times this quantity, i.e., 640 gm. of monosilicate, was therefore used in preparing the size. 1 gm. of rosin was stirred in the cold with 640 gm. of monosilicate solution, and then made up to 1,000 c.c. with hot water. No trace of silica was precipitated. The solution then contained in addition to 1 gm. of rosin, 22.40 gm. of silicic acid.

*Expt. 33.*—Size prepared as above. The amount added corresponds to  $\frac{1}{2}\%$  of rosin on the dry pulp.

250 c.c. of size were added to 2 litres of pulp (= 50 gm. air-dried material). After stirring for half an hour the mixture was precipitated with 205 c.c. of 10% alum solution. 250 c.c. of size in the absence of fibre use up 180 c.c. of alum solution, so that 205 c.c. gave an acid reaction. After a further half hour's stirring, the mixture was filtered. The wash water was milky; it was therefore added again to the pulp and treated with 100 c.c. of alum solution. The total amount of alum used was consequently 305 c.c. of 10% solution. The reaction of the pulp was strongly acid. After a quarter of an hour's stirring, the pulp was again filtered, washed and sampled. The wash water was clearer, but still milky.

Determination of silica in the wash water gave 2.5486 gm.  $\text{SiO}_2$ . Thus 46% of the  $\text{SiO}_2$  had passed into the wash water, 54% remaining in the pulp.

The absorption of silica by the pulp was therefore 6.10% of the weight of the pulp.

*Properties of the Paper.*—Strength: The breaking length



was 2,300 m., no less than 1,300 m. under that of the unsized paper. The extension had diminished by about 1% to 2.09%.

Handle and rattle: Not much better than with plain rosin sizing.

Colour: White as that of the original pulp.

Resistance to ink: Standard ink showed through distinctly and ran somewhat.

Expt. 33 is therefore considerably less successful as regards strength and ink resistance. The large amount of aluminium sulphate required, together with the higher price of monosilicate, appears to render the use of this compound impracticable. •

SIZING BY THE METHOD OF G. SOMMER, OF REVAL (D.R.P. No. 257,816).—The second of the patents already mentioned in the introduction to this chapter depending on the use of silicate in conjunction with rosin is that of G. Sommer of Reval (Russia). This patent, No. 257,816, Kl. 55c, is dated March 13th, 1913, and the claim runs as follows:—

“Method of paper sizing in which rosin is mixed with bases or basic salts at a temperature so low that no silicic acid is set free, and characterised by the fact that the mixing is carried out in so dilute a solution that the mixture may be added directly to the pulp.”

Since Sommer gives no practical example in the patent specification, the following size mixture was prepared as a trial.

*Preparation of Size for Expt. 34.*—0.5 gm. of rosin, finely pulverised in a mortar was treated with a solution of 2.5 gm. 30° Bé. silicate in 220 c.c. of water (i.e., a very dilute solution). After some stirring, complete solution took place. No silicic acid separated. The dilution was about 1 in 85.

*Size for Expt. 35.*—0.5 gm. of rosin was dissolved in 230 c.c. of silicate solution containing 2.5 gm. of solid silicate (7.05 gm. 38° Bé. silicate). No separation of silica occurred. Dilution of silicate 1 in 33.

• In both cases an excess of alkali was present, so that all the rosin might be saponified.

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Sizing experiments were then carried out with the two preparations.

*Expt. 34.*—Size prepared as described. 1% rosin and 5% 38° Bé. silicate.

The size was added to 2 litres of pulp, corresponding to 50 gm. of air-dried material, and stirred for half an hour. It was then treated (weak acid reaction) with 25 c.c. of 10% alum solution, equivalent to 5% of crystal alum on the air-dry material. After a further half hour's stirring the mixture was filtered, washed and sampled. Examination of the wash water gave 0.2639 gm.  $\text{SiO}_2$ .

The amount originally added was 0.6399 gm. and thus 41% of the  $\text{SiO}_2$  passes into the wash water, 59% remaining in the pulp.

This represents fixation of 0.75% of  $\text{SiO}_2$  on the air-dry material.

*Expt. 35.*—Size prepared as described. 1% rosin and 5% silicate (calculated as anhydrous silicate).

The size was added to 2 litres of pulp, stirred for half an hour and treated with 35 c.c. of 10% alum solution ( $\approx$  7% crystal alum calculated on the dry material). After a further half-hour's stirring, the mixture was filtered, washed and sampled.

*Examination of the Wash Water.*

Used : 2.5 gm. anhydrous silicate = 1.8480 gm.  $\text{SiO}_2$ .

Found in wash water : 0.7031 gm.  $\text{SiO}_2$ .

Thus 38% of the  $\text{SiO}_2$  has passed into the wash water, 62% remaining in the pulp.

This represents fixation of 2.29%  $\text{SiO}_2$  on the dry material.

*Properties of the Paper produced in Expts. 34 and 35.*—  
Handle and rattle : Better than with pure rosin size.

Colour : White as the original material.

Resistance to ink : Standard ink does not run or show through.

A further experiment using half the amount of rosin was now carried out.

*Expt. 36.*— $\frac{1}{2}\%$  rosin and 5% anhydrous silicate.

Method as above. In order to give weak acid reaction on precipitation 41 c.c. 10% alum solution were used, corresponding to 8.2% of crystal alum on the dry pulp.

*Properties of the Paper.*—Strength: The breaking length of the sized paper was 4,260 m., about 60 m. higher than that of the unsized material. For the sake of comparison it may be mentioned that, when using  $\frac{1}{2}\%$  of pure rosin in the form of a free rosin emulsion, the strength of the sized paper was about 180 m. higher than that of the unsized paper. The extension had diminished by 0.47% to 3%.

Handle and rattle: Rather better than with pure rosin size.

Resistance to ink: Standard ink ran somewhat and showed through.

Capillary rise in one hour at 20° C.:

Water: Mean 21 mm.

Printing varnish: Mean 7.2 mm.

Colour: The colour was as white as that of the unsized material.

The use of free rosin emulsions is also mentioned in the patent specification, and for the sake of completeness an experiment on these lines was carried out.

*Expt. 37.*— $\frac{1}{2}\%$  rosin in the form of emulsion, and 5% anhydrous silicate.

25 c.c. of a 25% rosin emulsion, corresponding to 0.5 gm. of free rosin was mixed with 50 c.c. of a silicate solution containing 5 gm. of anhydrous silicate, and made up to 200 c.c. No separation of silicic acid was observed. The solution was clear and of a brown colour.

Two litres of pulp, containing 50 gm. of dry material, were treated with 100 c.c. of the above size solution. After stirring for half an hour the mixture was treated with 50 c.c. of 10% alum solution (= 7% crystal alum on the air-dry pulp). After another half hour's stirring, the mixture was filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle : Better than with pure rosin sizing.

Colour : White as the unsized paper.

Resistance to ink : Standard ink runs less than in Expts. 36 and 37, but still shows through.

The foregoing experiments show that the method of paper sizing protected by G. Sommer in D.R.P. No. 257,816 is suited for practical use.

An examination of the numerical results of all the rosin-silicate sizing experiments brings out once more the good values for strength obtained with sizes containing silicate. In particular, the superiority of the rosin-silicate size is shown with the loaded papers when only  $\frac{1}{2}\%$  of rosin is used. The reduction of breaking length from that of the normally sized and unloaded paper is here about 900 m. less than that of a loaded paper normally sized with 3% resin. At the same time about 4% more loading is retained.

Further, there is found an increase in the capillary rise of the paper sized with rosin and silicate, both in respect to water and to printing varnish. Papers which are sized only with rosin have also a considerable capillary action on printing varnish, with the result that the printing varnish dissolves the precipitated rosin size, thus diminishing the sharpness at the edge of the letters in printing, and so, especially in rapid printing, leading to a blurring of the type. In the rosin-silicate combination there is also a capillary action favourable to the penetration of aqueous solutions.

A great advantage of the use of silicate in combination with rosin consists in the greater whiteness of the paper produced, and in the fact that yellowing on exposure to daylight is, as far as has been seen up to the present, almost entirely prevented.

## CHAPTER III

### SILICATE AND FATTY ACIDS

THE use of fatty acids for sizing paper is ancient practice. Canson \* was the first who used stearic and other fatty acids for this purpose. Since even before the war these acids were costly, the author has used much cheaper varieties, viz., soya bean oil and cotton-seed oil (made by Henkel & Co., in Dusseldorf).

SAPONIFICATION OF THE FATTY ACIDS WITH SODA LYE.—According to information supplied by Henkel & Co., the fatty acids in question have the following characteristic properties.

Soya Bean Oil. | Cotton-seed Oil.

Melting point . . . . .	20°–30°	30°–40°
Saponification number . . . . .	198	203.9
Percentage free fatty acid . . . . .	92.73	88.79
Iodine number . . . . .	120–130	110–120
Acid number . . . . .	183.6	181

The saponification number of both oils was checked and can be taken as correct. It is expressed as a number of milligrams of potassium hydrate which are necessary for the saponification of 1 gm. of an oil or wax.

*Soya Bean Oil Soap.*—The saponification number shows that 19.8 gm. of potassium hydroxide, or 14.12 gm. of sodium hydroxide are necessary for the saponification of 100 gm. of the soya bean oil.

. 20 gm. of the above oils were saponified, requiring a

\* Hofmann's "Handbuch der Papierfabrikation," II., Aufl., 1895, Bd. II. 6.

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nominal 2.824 gm. of sodium hydroxide, or 29.5 c.c. of a 9.6% solution of caustic soda.

The operation was carried out in a porcelain dish on a water bath, with continual stirring.

The resultant soap solution was dissolved in hot water and made up to 1,000 c.c. in a measuring flask. The colour of the solution was bright brown.

100 gm. of the cotton-seed oil required :—

14.54 gm. of sodium hydroxide ; or

20.39 gm. of potassium hydroxide.

20 gm. of material were treated with 30.3 c.c. of the above approximate 10% caustic soda solution.

The procedure adopted was exactly the same as that for the soya bean oil.

After standing for some hours, the solution gradually became bright yellow and gelatinous. A slight warming of the flask, however, was sufficient to dissolve the soap, and keep the mass liquid for several hours.

(a) SIZING WITH NORMAL SODIUM SOAPS OF FATTY ACIDS.—For the sake of comparison with the later experiments on sizing with various combinations of silicate and soap, experiments were first made, using the soaps of the above fatty acids alone.

*Sizing with Soya Bean Oil Soap.*—Expt. 38.— $\frac{1}{2}$ % soya bean oil in the form of a soda soap.

To 2 litres of pulp, containing 40 gm. of air-dried cellulose, were added 10 c.c. of a soap solution containing the equivalent of 0.2 gm. of soya bean oil, the whole being stirred for half an hour. The pulp was then treated with 17 c.c. of a 10% aluminium sulphate solution to weakly acid reaction. After a further half hour's stirring, it was filtered, washed and sampled.

*Properties of the Paper.*—The breaking length was 4,420 m., about 280 m. less than that of the unsized paper (4,700 m.). The extension showed an unexpected decrease of 0.13% to 3.17%.

**Handle and rattle:** Similar to that of the original paper.

**Colour:** Yellowish compared to the unsized paper.

**Resistance to ink:** Standard ink neither blotted nor penetrated. The writing was, however, fairly visible on the other side.

**Capillary rise:** In one hour at 20° C.:

Water: Mean 0.0 mm.

Printing varnish: Mean 7 mm.

*Expt. 38A.*— $\frac{1}{2}\%$  soya bean oil in the form of soda soap.

In this experiment, the same quantity of soap was used, and precipitated by an increased quantity of aluminium sulphate solution, viz., 25 c.c. corresponding to 6.25% of crystal alum, calculated on the air-dried weight of the cellulose. The reaction of the mixture was then strongly acid. The subsequent procedure was as above.

*Properties of the Paper.*—In comparison with Expt. 38, the colour was somewhat brighter, but not so good as that of the untreated material.

*Expt. 39.*—1% soya bean oil as soda soap.

To 2 litres of pulp containing 40 gm. of air-dried cellulose were added 20 c.c. of soap solution corresponding to 0.4 gm. of soya bean oil, and after treatment as above there were added a further 18 c.c. of aluminium sulphate solution to weakly acid reaction.

*Properties of the Paper.*—Handle and rattle: Not so good as that of the unsized paper.

**Colour:** Yellow when compared to the original unsized paper.

**Ink resistance:** Standard ink did not blot or penetrate, but the visibility of the writing on the reverse side was objectionable. The samples picked up the ink badly, and were sensitive to the pressure of the pen.

*Expt. 40.*— $2\frac{1}{2}\%$  soya bean oil in the form of soda soap.

This experiment was carried out as above except that proportionately greater quantities of oil were used

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The sizing materials were added to 110 gm. of air-dried pulp until a weakly acid reaction was obtained.

Sampling the pulp was interfered with by excessive frothing.

*Properties of the Paper.*—Handle and rattle : Markedly inferior to the unsized product, quite flabby.

Colour : Decidedly yellow.

Resistance to inks : Ordinary inks did not run or blot.

The visibility of the writing from the back of the paper is, however, unsatisfactory. The sample sheets took ink badly and their surfaces were too easily marked by a pen.

Capillary rise in one hour at 20° C. :

Water : Mean 0.0 mm.

Printing varnish : Mean 7 mm.

*Sizing Experiments with Cotton-seed Oil.*—Experiments were carried out using similar quantities of cotton-seed oil to those taken in the previous soya bean oil series.

*Expt. 41.*— $\frac{1}{2}$ % cotton-seed oil as soda soap.

*Properties of the Paper.*—Strength : Here, as in the soya bean oil experiments, the tensile strength fell off by 260 m. to a value of 4,440 m.

The stretch fell 0.15 to 3.15%, a negligible change.

Handle and rattle : Practically the same as in the unsized material.

Colour : Yellow compared with the white of the unsized material.

Resistance to inks : Ordinary inks did not run or blot. The paper, however, was somewhat translucent.

Capillary rise in one hour at 20° C. :

Water : Mean 0.0 mm.

Printing varnish : Mean 7 mm.

*Expt. 41A.*— $\frac{1}{2}$ % cotton-seed oil as the soda soap.

This experiment is similar to 38A, inasmuch as a large quantity of aluminium sulphate was used, and a strongly acid pulp. 25 c.c. of the 10% aluminium sulphate solution were employed.



*Expt. 42.*—This experiment is exactly similar to Expt. 39.

*Expt. 43.*—2½% cotton-seed oil as soda soap.

This experiment corresponds exactly to No. 40 which was carried out with soya bean oil soap. The properties of the paper produced were similar to those obtained in Expts. 40 and 39.

To conclude the series of sizing experiments with the soda soaps, an experiment with 5% of cotton-seed oil was carried out in order to show how the ill effect of the fatty acids in respect to strength, handle, rattle and the writing qualities of the paper increases with increasing amounts of these materials.

*Expt. 44.*—5% cotton-seed oil as the soda soap:

Two litres of pulp containing 40 gm. of air-dried cellulose were added to 100 c.c. of a soap solution containing 2 gm. of cotton-seed oil. The whole was well stirred, and after half an hour, 25 c.c. of aluminium sulphate solution containing 6.25% crystal aluminium sulphate on the weight of the air-dried pulp were added. After a further half an hour it was drained, well washed, and then sampled. The frothing which took place was so great that a little alcohol had to be added to prevent it.

*Properties of the Paper.*—Strength: The breaking length fell by 1,650 m. to 2,150 m. when compared with the unsized paper. The stretch went down by 2.07% to 1.67%.

Handle and rattle: The paper was quite soft with woolly surface.

Resistance to inks: The paper took up hardly any ink, and was particularly sensitive to pen pressure. The ink was easily visible from the back of the paper.

Colour: Yellow.

Capillary rise in one hour at 20° C.:

Water: Mean 0.0 mm.

Printing varnish: Mean 8 mm.

Expts. 38 to 44 have, therefore, shown that the use of soya bean oil and cotton-seed oil soaps for the sizing of paper

should not exceed 1%, beyond which the strength, handle, rattle and general printing qualities of the paper are markedly affected and the deterioration is, moreover, a loss to be added to cost of material.

The above statements are also confirmed by Klemm in his lecture on "The Problem of Rosin Substitutes," where, speaking of fats and waxes, he says that their small effect in comparison to that of rosin is to be ascribed to their low melting-points (between 20° and 40° C. in the cases considered), especially in view of the sintering phenomena which rosin exhibits when paper containing it is heated on the drying cylinders.

(b) SIZING WITH SODA SOAPS OF FATTY ACIDS CONTAINING EXCESS OF ALKALI.—A few experiments are interpolated here which, although they are not immediately concerned with silicate sizing, have a certain bearing upon it.

If a completely saponified soda soap which has been made with sodium hydroxide is brought into distilled water its solution is clear; if caustic soda is now added a precipitate is formed locally which disappears on stirring: when sufficient caustic has been added, however, a precipitation of "anhydrous soap" takes place owing to the diminution of the hydrolysis of the soda soap.

On the addition of soap solution to water of about nine or ten German degrees of hardness, a precipitation takes place, probably of the calcium soap. If caustic soda is also added, a large precipitate of sodium soap is produced.

The above phenomena were quantitatively illustrated by two titrations:—

(1) To 180 c.c. of distilled water were added, by means of a pipette, 10 c.c. of soap solution. 40% caustic soda solution was then run in from a burette until a permanent precipitate was obtained. 9.1 c.c. were required.

(2) 180 c.c. of tap water (10° hardness) were treated as above, and only 5.9 c.c. of caustic soda were required to produce a permanent precipitate.

The formation of calcium soap in hard water, therefore, appears to be of some importance.

In the course of another experiment both of the fatty acids already used were saponified with fourteen times the calculated quantity of caustic soda solution. These strong alkaline solutions gave with tap water an immediate separation of calcium soap, together, probably, with some sodium soap. If the requisite quantity of aluminium sulphate (preferably estimated by titration) were first added to the tap water before the separation of the sodium soap, one might reasonably expect that the separation of "aluminium soap" would take place immediately on the addition of the fatty acid.

In the following experiments this reaction was examined. In some cases the soap, and, in others, the aluminium sulphate solution, was first added to the pulp.

*Expt. 45.*—0.5% soya bean oil saponified with fourteen times the calculated quantity of sodium hydroxide.

Two litres of pulp containing 50 gm. of air-dried cellulose were mixed with 25 c.c. of soap solution containing 0.25 gm. of soya bean oil, stirred for half an hour, and then mixed with 33 c.c. of aluminium sulphate solution (equivalent to 6.6% crystal alum calculated on the air-dried substance) till the reaction of the pulp was slightly acid. After a further half hour the pulp was filtered, washed and sampled.

*Properties of the Paper.*—Handle and rattle: The same as in the unsized sample.

Colour: Nearly as white as the unsized sample.

Resistance to inks: Standard inks ran and blotted somewhat.

Capillary rise in one hour at 20° C.:

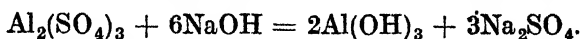
Water: 27 mm.

Printing varnish: 8 mm.

These changes, unfavourable as far as ink resistance is concerned, may be ascribed to the formation of aluminium hydroxide.

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The existence of a large quantity of free alkali brings about the following reaction with the aluminium sulphate:—



The sodium sulphate is removed on washing. The effect of aluminium hydroxide is treated more fully later, when dealing with silicate and animal glue.

The clear white tint of this sample, compared with that of paper sized with the normally saponified fatty acids, is due to the filling action of the white aluminium hydroxide that is deposited.

*Expt. 45A.*—As *Expt. 45*, except that the aluminium sulphate was added before the soap.

*Properties of the Resultant Pulp.*—Except for the ink-resistance the properties were the same. The ink-resistance was considerably better than that obtained in the foregoing experiment: the ink ran less although it showed through to some extent.

*Expt. 46.*—0.5% cotton-seed oil with fourteen times the calculated quantity of caustic soda.

The procedure was the same as in *Expt. 45*.

*Expt. 46A.*—Procedure as in 46, except that the aluminium sulphate was added before the cotton-seed oil.

*Properties of the Paper.*—The phenomena observed in *Expts. 45* and *45A* were shown in *Expts. 46* and *46A* somewhat more markedly. Two parallel experiments were now made, using more soap.

*Expt. 47.*—2% soya bean oil with fourteen times the calculated quantity of sodium hydroxide.

The same quantity of pulp as before was sized with 2% soya bean oil in the form of its soda soap and then mixed with 58 c.c. 10% aluminium sulphate solution. (That is, 11.6% crystal alum to the air-dried substance.)

*Expt. 47A.*—The same quantities were used as in *Expt. 47*, but first the aluminium sulphate and then the soap was added to the pulp.

*Properties of the Paper.*—In this case there was no differ-

ence in the ink resistance. In both samples the ink ran, and after a time penetrated the sheet, evidence of the bad effect of the aluminium hydroxide formed by the high percentage of soap in the size.

*Summary.*—Expts. 45 to 47A lead to the conclusion that when the soap is added before the aluminium sulphate a calcium soap is formed in addition to the aluminium soap: on reversing the procedure, however, the aluminium soap alone is formed. When small quantities of soap ( $\frac{1}{2}\%$ ) are used the two methods, therefore, give different results, but with larger amounts (2%) the proportion of calcium soap formed is too small in comparison with the aluminium soap for any difference to be shown.

The bad effect of aluminium hydroxide on the ink-resistance of the paper must again be emphasised.

SIZING WITH THE SODA SOAP OF FATTY ACIDS IN CONNECTION WITH SODIUM SILICATE.—*Expt.* 48.—0.5% of the soda soap of soya bean oil (see Expt. 38), and 5% sodium silicate.

To 2 litres of pulp (= 50 gm. air-dry cellulose) were added 12.5 c.c. of soap solution (= 0.25 gm. soya bean oil), and 25 c.c. dilute sodium silicate solution (= 2.5 gm. 38° Bé.). The whole was stirred for half an hour with 36 c.c. aluminium sulphate solution (giving 7.2% aluminium sulphate in respect to the dry material). Finally the mixture was filtered, washed and sampled.

An analysis of the washing water gave 0.5400 gm. silicic acid.

The original amount used was 0.6550 gm., so that 82% silicic acid has passed into the wash water and 18% into the pulp.

Calculated on the dry material this is equivalent to a fixation of 0.23% silicic acid.

*Properties of the Paper.*—Strength: The breaking length (3,890 m.) was 90 m. higher than that of the unsized sample, while the stretch (3.4%) was 0.28% lower.

Handle and rattle: Better than in the unsized sample.

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Capillary rise in one hour at 20° C. :

Water : 32 mm.

Printing varnish : 7.3 mm.

The increased capillary rise for water is an obvious effect of the addition of the silicate.

Colour : White like the unsized material.

*Expt. 49.*—0.5% cotton-seed oil and 5% sodium silicate solution 38° Bé. The procedure was the same as in Expt. 48, except that cotton-seed oil was used.

Analysis of the wash water gave 0.6336 gm. silicic acid.

Since 0.6550 gm. was originally taken, this gives 97% silicic acid in the washing water, and 3% in the pulp, corresponding to 0.043% silicic acid in the air-dried material.

*Properties of the Paper.*—Strength : The breaking length (3,800 m.) was the same as that of the unsized paper. The stretch (3.45%) was 0.23% greater than that of the unsized paper.

Handle and rattle : Good, like that of the unsized paper.

Colour : White.

The following experiment was designed to show the effect produced by first precipitating the silicate, subsequently adding the soap and again precipitating :—

*Expt. 50.*—5% sodium silicate (38° Bé.) added first and then 0.5% soap. The pulp was mixed with the diluted silicate and stirred for a quarter of an hour after adding aluminium sulphate solution : then followed the addition of the cotton-seed oil and another fifteen minutes' stirring after adding the corresponding quantity of aluminium sulphate solution to a faintly acid reaction : the whole was then stirred for another half hour, filtered, washed and sampled.

*Properties of the Paper.*—There was no appreciable difference between this and Expt. 49.

In the following experiment the amount of silicate was further increased to 10% the amount of soap remaining the same.

*Expt. 51.*—10% sodium silicate 38° Bé. and 0.5% soya

bean oil. The procedure was exactly the same as before : the soap and sodium silicate were added to the pulp together, and then precipitated with 40 c.c. of 10% aluminium sulphate solution (corresponding to 8% crystal alum). The mixture was then filtered, washed and sampled.

*Properties of the Paper.*—The paper had good handle and rattle, and was quite as white as the original material.

To show the good effect of silicate in preventing flabbiness of the paper the following experiment was carried out. This experiment is parallel to No. 44, which shows clearly the bad effect of 5% fatty acid in the form of soda salt with regard to the strength, handle and rattle of the paper. (In practice, the conditions of this experiment would, of course, never obtain.)

*Expt. 52.*—5% cotton-seed oil as soda soap, and 15% silicate 38° Bé.

The pulp was first mixed with the soap, next treated with aluminium sulphate, then with silicate, and finally with more aluminium sulphate. The quantity of aluminium sulphate added corresponded to 10% of crystal alum calculated on the air-dried material.

*Properties of the Paper.*—Strength : The breaking length (4,000 m.) was 200 m. better than that of the unsized paper. The stretch had fallen 0.75% to 2.93%.

Handle and rattle : The same as that of the unsized paper.

Colour : Yellowish.

Ink resistance : Standard ink ran and blotted slightly : the paper was easy to write on and had a good surface.

Capillary rise in one hour at 20° C. :

Water : 15 mm.

Printing varnish : 6.5 mm.

This experiment showed clearly the positive effects of sizing with silicate, in relation to strength, handle and rattle of the paper. The tensile strength (2,350 m.), of the paper from Expt. 52, is nearly 2.5 times as great as that obtained in Expt. 44 where 5% fatty acid only was added. The paper

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also had good handle and rattle in contrast to the flabbiness obtained in Expt. 44.

**SIZING WITH AN OIL SAPONIFIED WITH SODIUM SILICATE.**

—The saponification was carried out as in the case of rosin. Soya bean oil was first treated with just so much silicate as to furnish the alkali equivalent of the fatty acid of the oil.

100 gm. of soya bean oil were found to use 14.12 gm. of sodium hydroxide, that is, 10.94% of  $\text{Na}_2\text{O}$ . Direct analysis of trisilicate showed 100 gm. to contain 7.912 gm. of  $\text{Na}_2\text{O}$ , so that 10.94 gm. would be obtained from 138.27 gm. silicate.

20 gm. of soya bean oil were mixed in the cold with 27.645 gm. of 38° Bé. silicate, and kneaded with a pestle while being warmed on the water bath. Warm water was then added, and the whole boiled up. The final volume was made up to 1,000 c.c.

At the bottom of the vessel there was a thick, finely-divided precipitate of silicic acid. The solution became pale yellow and slightly turbid on standing. 100 c.c. were pipetted out and analysed for silicic acid in the usual way. No trace of silicic acid was found, showing that removal of the alkali causes complete precipitation.

For the sake of completeness, an experiment was carried out with the size so prepared. The liquor was not shaken before use.

*Expt. 53.*—0.5% soya bean oil completely saponified with silicate.

The experiment was carried out with the same quantities of pulp and in the same way as before.

*Properties of the Paper.*—Strength: The breaking length (4,450 m.) was 250 m. greater than that (4,700 m.) of the untreated pulp. The stretch, however, showed a diminution.

Handle and rattle: The same as that of the original pulp.

Colour: Slightly yellow compared with that of the original pulp.



**Ink resistance :** Ordinary ink did not run, but the writing showed fairly strongly through the paper.

The properties of the paper are comparable with those obtained in Expt. 38, where the fatty oil was saponified with caustic only.

As was done in sizing with rosin, the proportion of silicate was now raised some fourteen times.

5 gm. of soya bean oil were saponified as before with 97 gm. of 38° Bé. silicate (which is about fourteen times the quantity used in Expt. 53), and the volume was made up to 1,000 c.c. Very much less precipitate was formed.

20 c.c. of the clear solution were analysed as before for silicic acid ; 0.4929 gm. was found, so that the 1,000 c.c. contained 24.6450 gm.  $\text{SiO}_2$ .

In the 97 gm. of 38° Bé. silicate used for the saponification the silicic acid, according to analysis, amounts to 25.41 gm., and, therefore,  $25.41 - 24.65 = 0.76$  gm. silicic acid was precipitated in the saponification, or only 3% of the amount used.

97% of the silicic acid remained in the solution.

An experiment was carried out with this size by way of completing the series.

*Expt. 54.*—0.5% soya bean oil with fourteen times the quantity of silicate required for saponification.

The procedure was the same as before. The properties of the pulp were similar to those obtained in Expt. 51, where soap was added instead of silicate.

It now seemed advisable to add more silicate. 5 gm. of soya bean oil were saponified with 150 gm. of silicate (about twenty-one times the alkalinity necessary to saponify the fatty acids) and the mixture made up to 1,000 c.c.

The appearance of the size solution was cloudy, but there was no precipitate and none formed on standing.

1,000 c.c. of the solution were found by analysis to contain 39.32 gm. silicic acid.

According to the analysis of silicate by v. Baerle & Co. (see above), silicate of 38° Bé. contains 26.20 gm. silicic acid per 100 gm., so that there are in 150 gm. 39.37 gm.

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"Silicate soap" can thus be prepared in the cold by the union of the requisite amounts of silicate and fatty acid. The size is then put into the Hollander in this form, where it dissolves and distributes itself through the large volume of water, and is then precipitated with alum.\*.

*Expt. 55.*—0.5% soya bean oil saponified with twenty times the required quantity of silicate.

The sizing was carried out with 50 c.c. soap solution = 0.25 gm. soya bean oil and 7.5 gm. silicate solution 38° Bé., the mixture being precipitated with 33 c.c. of a 10% aluminium sulphate solution (equivalent to 6.6% crystal alum calculated on the air-dried pulp).

Calculating on the air-dried cellulose, there were added 0.5% soya bean oil and 15% silicate of 38° Bé. strength.

*Properties of the Paper.*—Strength: The breaking length (3,800 m.) was the same as that of the unsized material. The stretch (3.40%) had fallen off by 0.28%.

Handle and rattle: Better than that of the unsized material.

Capillary rise in one hour at 20° C.:

Water: 35 mm.

Printing varnish: 7.5 mm.

Colour: White, like that of the unsized material.

With regard to the saponification by means of silicate, it was advisable to perform a similar experiment on direct saponification in the pulp, seeing that the melting-points of soya bean oil and cotton-seed oil lie close together at the low temperatures of 20° to 30° and 30° to 40° respectively. In such a case, using an amount of silicate insufficient for complete saponification, the silica precipitated should remain in the pulp as a filling material.

\* \* The above-mentioned silicate-oil soap, with the silicate-rosin soap already described, is protected by the author under D.R.P., No. 320,829, "The Preparation of Silicate Soap." In the further patent specifications for this process the viscous silicate soap is brought to a nearly dry condition by the addition of filling material, thus facilitating transport in cheap packages. In a fourth claim, the addition of a dry precipitating agent (e.g., acid salt) is protected. This salt exerts its precipitating action as soon as solution takes place in the Hollander.

*Expt. 56.*—0.5% soya bean oil completely saponified in the pulp with water glass.

Two litres of pulp containing 50 gm. of the air-dried material were warmed to 40° on the water bath, and then 0.25 gm. of soya bean oil was added and the whole stirred rapidly. When the temperature had risen some degrees, a quantity of silicate was added just sufficient for complete saponification of the oil (*Expt. 53*). After half an hour's stirring, the mixture was precipitated while still at 40° with aluminium sulphate.

*Properties of the Paper.*—The paper had good handle and rattle, and was much the same as the paper sized with soap and silicate, but with a fainter colour.

Ordinary ink ran and blotted considerably, proof that the whole of the silicate was taken up by the pulp, for the 0.5% soya bean oil soap would not have made the ink run. (See *Expts. 38 and 53*.)

In practice, saponification in the Hollander would be uneconomical owing to the cost of heating the pulp to 40°.

The experiments on sizing with silicate and fatty acid were brought to a conclusion by an experiment in which soya bean oil was saponified with the monosilicate of metasilicic acid.

It has been seen that 100 gm. of soya bean oil require 14.12 gm. NaOH (*i.e.*, 10.94 gm. Na<sub>2</sub>O) for complete saponification.

It was found that 100 gm. of monosilicate contained 3.621 gm. Na<sub>2</sub>O. Hence 100 gm. of fatty acid require 302.13 gm. of monosilicate, or 20 gm. require 60.43 gm., for complete saponification.

20 gm. of soya bean oil were, therefore, mixed with 60.43 gm. of the monosilicate (equivalent to 120.86 gm. of the prepared solution) and warmed on the water bath, then diluted with warm water and further warmed. The volume was finally brought up to 1,000 c.c.

A similar result was again obtained, as was to be expected: the whole of the silicic acid was precipitated as with the

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trisilicate of metasilicic acid. 50 c.c. of the pale yellow, slightly turbid size solution showed no trace of silicic acid on analysis.

An experiment was carried out with the clear upper portion of the size solution.

*Expt. 57.*—0.5% soya bean oil completely saponified with monosilicate, and precipitated with aluminium sulphate amounting to 5% of crystalline sulphate on the air-dried material.

*Properties of the Paper.*—Strength: The breaking length (4,435 m.) had fallen off by 265 m. from that of the original material. The stretch showed no noticeable decrease.

Handle and rattle: The same as that of the original material.

Colour: Pale yellow compared to that of the original material.

Ink resistance: Ordinary ink neither ran nor blotted, but the writing showed through very strongly.

The above properties corresponded closely with those obtained in Expt. 38 (complete saponification with NaOH) and those obtained in Expt. 53 (complete saponification with trisilicate), as was to be expected.

Finally, it should be mentioned that in connection with the patent of G. Sommer, of Reval (D.R.P., No. 257,816, see above), an attempt was made to saponify the fatty oils in cold, very dilute silicate solution. It was not found possible to break up the fat sufficiently finely with a glass rod to obtain an emulsion (as has been done in the case of rosin). If the fat were melted to obtain better mixing, it immediately solidified on contact with the cold silicate solution.

It should, however, be possible to obtain an emulsion of fatty acid in very dilute water glass solution with the help of a mechanical emulsifier.

This also holds for D.R.P., No. 320,829 [the introduction of fatty acids into an excess of silicate]. Here also, for cold saponification, the fatty acid should be introduced in a

sufficiently fine state of division through the jet of the emulsifier into the undiluted of 38° to 40° Bé. silicate.

On looking back over the results obtained in the experiments on sizing with silicate and fatty acids, and with fatty acids alone, the increase of tensile strength in the case of treatment with silicate is very clearly seen. The action of the silicate is brought out particularly strongly in the case of 5% fatty acid, where the use of silicate has increased the tensile strength by 86% over that obtained with pure fatty acid size, to say nothing of the better handle and rattle.

An experiment that is particularly noteworthy is that with silicate and silicate soap, according to D.R.P., No. 320,829, for the use of only 0.5% fatty acid would keep the cost within normal limits. For cheaper papers one could increase the ratio of silicate to fatty acid.

It will be seen that, as with the silicate-rosin mixture, the absorptive capacity of the paper was raised by the use of silicate.

## CHAPTER IV

### SILICATE AND ANIMAL GLUE

As already mentioned in the introduction, Ernst Altmann has D.R.P. (No. 28,375, February 29th, 1915), on the application of a suspension of talc in gelatine to the preparation of paper size, and later another patent (No. 288,106) broadening the above, on the application of a suspension of talc in gelatine and soda. It is a question, in the first place, of the flocculation of the hydroxides of silicon and magnesium contained in the hot talc paste, and, in the second place, of the flocculation of the alkali silicates formed by the alkali carbonate as a very soluble gelatinous mass of hydrated silica.

This method of sizing will be considered at the end of this chapter. But the more favourable effect of talc as a loading compared with that of china clay, observed in Chapter I. of this work (Expts. 3D, 3D', 3D''), may be pointed out here.

Quite independently of these, experiments were carried out in which a combination of animal glue and silicate was used as a sizing agent.

**PRELIMINARY EXPERIMENTS.**—To a solution of animal glue a quantity of silicate was added, and then 10% aluminium sulphate solution, until the reaction was slightly acid; a thick flocculent precipitate appeared; no further precipitate was produced in the filtrate with tannin. All the animal glue had, therefore, been precipitated by the silicate.

\* In a second experiment, in which animal glue solution was mixed with aluminium sulphate alone, no visible precipitate was found, yet on the addition of tannic acid a precipitate appeared.

These observations suggested that a systematic series of precipitations, at the same degree of dilution should be carried out. To avoid errors, the following facts were first established :—

(a) Silicate solution gave no precipitate with tannin.

(b) Aluminium solution mixed with tannin gave no precipitate.

(c) Silicate solution much diluted with aluminium sulphate solution gave a white cloudiness, but there was no precipitate or flocculation on the addition of tannin solution.

(d) Silicate and animal glue mixed gave a precipitate with tannin.

(e) Some unsized pulp was filtered off on a fine sieve and the filtrate treated with tannin; this produced neither a precipitate of organic matter nor a coagulation of the fine filaments in the filtrate from the pulp.

*Precipitation Experiments.*—(1) Two litres of tap water in a measuring cylinder were treated with 10 c.c. of a 5% solution of glue, corresponding to a 1% sizing, and then with aluminium sulphate solution, until the reaction was acid; no visible precipitate was formed until the addition of tannin.

(2) Proportions as in experiment (1), but 5 c.c. of silicate solution were added before precipitation with aluminium sulphate solution. Only a slight cloudiness appeared in the acid solution, but precipitation occurred on the addition of tannin.

(3) Proportions as in experiment (2), but 25 c.c. of silicate solution (= 5% water glass) were added. Aluminium sulphate produced only a thick turbidity, and the addition of tannin was required to produce flocculation.

(4) As in experiment (3), but with 50 c.c. silicate solution, corresponding to 10% silicate. On adding aluminium sulphate until the reaction was acid a heavy flocculent precipitate appeared. On treating the filtrate with tannin, it gave a slight cloudiness which did not coagulate on boiling. There was hardly any gelatine in the filtrate.

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(5) 20 c.c. of animal glue, corresponding to 2% sizing, were used; the other quantities were the same as in experiment 4. A precipitate was formed in the acid solution, but did not settle out entirely; the cloudy filtrate gave a fairly heavy precipitate with tannin.

(6) Two litres of tap water were again treated with 20 c.c. of animal glue solution (= 2%), then with 75 c.c. silicate solution, corresponding to sizing with 15% silicate, and finally with aluminium sulphate, until the reaction was acid. A heavy precipitate was immediately formed, which settled out leaving a clear solution. In the clear filtrate no gelatine could be found on treating with tannin, even after boiling.

These experiments show that, with correct proportions of animal glue and silicate, and using sufficient of the latter, complete precipitation of the glue together with silica can be brought about by aluminium sulphate.

The following sizing experiments were next carried out:—

**SIZING WITH ANIMAL GLUE.**—*Expt. 58.*—2% animal glue alone, unprecipitated.

Two litres of pulp (= 50 gm. of air-dried material) were treated with 20 c.c. of a 5% animal glue solution (= 1 gm. glue), stirred for an hour, and then filtered, washed and sampled.

On treating the 2 litres of filtrate with tannin, there was a heavy precipitate, and the glue could still be readily detected even in the wash water.

*Properties of the Paper.*—No appreciable difference from the original material was produced.

Capillary rise in one hour at 20° C.:

Water: 17 mm.

Printing varnish: 6 mm.

*Expt. 59.*—2% animal glue and aluminium sulphate.

The amounts of pulp and glue were the same as in *Expt. 58*, but after stirring for half an hour 20 c.c. of 10% aluminium sulphate solution were added, i.e., 4% of crystal alum referred to the air-dried material.



*Waste Liquor.*—In the filtrate from the washing of the material only a slight precipitate was observed on treating with tannin. On boiling, the precipitate became rather more obvious. The ash content of the paper was determined in order to find the absorption of loading in future experiments. The ash amounted to 0.87%.

*Properties of the Paper.*—Strength: The breaking length was 5,975 m., compared with 5,600 m. for paper sized with glue and 4,600 m. for the unsized paper. The stretch was 2.98%, which is 0.21% higher than for the unsized paper.

Handle and rattle: Considerably better than for the unsized paper.

Colour: Rather dull compared with the unsized material.

Resistance to inks: Ordinary inks did not run to any extent, but penetrated in some places.

Capillary rise in one hour at 20°:

Water: 9 mm.

Printing varnish: 6 mm.

*Expt. 60.*—5% animal glue with aluminium sulphate. 50 c.c. of a 5% glue solution (= 2.5 gm. air-dried glue) were added to the same amount of pulp as in Expt. 58.

Precipitation was effected by 25 c.c. of aluminium sulphate solution, i.e., 5% of crystal alum on the dry material.

Considerable amounts of glue were precipitated by tannin from the filtrate. Even in the wash water a certain amount could be detected.

*Properties of the Paper.*—Strength: The breaking length had risen to 5,975 m., as compared with 5,600 m. for paper sized with 2% of glue and 4,600 m. for the unsized paper. The stretch was 2.98%, or 0.21% higher than for the unsized paper.

Handle and rattle: Considerably better than for the unsized sample.

Colour: Dull compared with the unsized paper.

Resistance to ink: Standard ink did not run, but penetrated the paper in some places. The additional expenditure

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of glue is out of proportion to the improvement in ink resistance.

Capillary rise in one hour at 20° C. :

Water : 5.75 mm.

Printing varnish : 6 mm.

SIZING WITH SILICATE AND GLUE.—*Expt.* 61.—2% glue and 10% silicate of 38° Bé.

The quantities of pulp and glue were the same as in *Expt.* 59, but 10% of silicate (referred to the air-dried material) was added to the pulp in addition to the glue, and after stirring for half an hour the mass was precipitated with 10% crystal alum.

In the filtrate traces of gelatine were present.

*Estimation of Silica.*—The analysis of the waste liquor was not possible, owing to the breaking of the evaporating basin. The silica content of the paper was, therefore, estimated from its ash value in comparison with that of the paper made in *Expt.* 59.

For this and for future estimations of the loading the ash of the paper was determined, and found to be 2.43%.

Subtracting from this ash content of 2.43% the 0.87% of ash of the paper sized with 2% animal glue alone in *Expt.* 59, we obtain a difference of 1.56 gm., which can be attributed to the silica content. Since the sizing material consisted of 2% animal glue with 10% water glass containing 26.20% silica, the proportion of the silica fixed is 59.60%.

Accordingly, about 60% of the silica occurs in the material, and about 40% in the waste liquor. The amount of silica absorbed by the paper amounts to about 1.56% of the air-dried material.

In all probability the amount of silica absorbed should be slightly lower, since a small portion of the ash must be attributed to aluminium hydroxide formed on precipitation, and to the increased absorption of animal glue. The amount of silica retained is, however, about 20% greater with the

silicate-glue size than when 10% of 38° Bé. silicate alone was used. In the latter case (Expts. 2 and 2A) only 46% of silica was retained, against 60% in the present experiment.

Strength: The breaking length was 5,680 m., an increase of 1,080 m. over that of the unsized paper, and so rather higher (80 m.) than in the application of animal glue and aluminium sulphate alone (Expt. 59). The stretch was 2.64%, a drop of 0.13% compared with that of the unsized paper.

Handle and rattle: Very good.

Capillary rise in one hour at 20° C.:

Water: 15 mm.

Printing varnish: 6.60 mm.

Colour: White, like that of the unsized sample.

*Expt. 62.*—5% animal glue and 20% of 38° Bé. silicate.

The quantities of pulp and glue were the same as in Expt. 60, but with the animal glue was mixed 20% of silicate solution of 38° Bé., referred to the air-dried material, and then precipitation was carried out with 95 c.c. aluminium sulphate solution (i.e., 17% crystal alum).

In the filtrate, before washing, a slight precipitate was produced with tannin; in the wash water itself no precipitate appeared, even on boiling, whereas in Expt. 60 (where 5% of animal glue was precipitated alone) a considerable amount remained in the filtrate, and a precipitate even appeared in the wash water.

Capillary rise in one hour at 20°:

Water: 14 mm.

Printing varnish: 6.6 mm.

In order to study the influence of silicate and animal glue, and of animal glue alone, on the fixation of loading, the following experiments were now carried out:—

*Expt. 63.*—2% glue and 20% of talc with aluminium sulphate.

The glue and the talc were mixed together on a water

bath at 70°, and then poured hot into the pulp; the mass was precipitated with 4% crystal alum, referred to the air-dried material, as in Expt. 59.

Only quite small amounts of glue could be detected in the filtrate by boiling with tannin.

The amount of ash found on ignition was 13.12%.

This 13.12% of ash contains  $13.12 - 0.87 = 12.25\%$  of ignited talc, since 0.87% of the sized but unweighted paper was ash (Expt. 59). 12.25% of ignited talc corresponds to 13.38% of unheated talc. Thus there was 13.38% of talc in the paper, or 67% of the amount taken.

*Properties of the Paper.*—Strength: The breaking length was 4,430 m., which is 170 m. less than that of the unsized and unweighted paper. The stretch was 2.6%, which is 0.17% less than that of the unsized paper.

Handle and rattle: Worse than for the unsized and unweighted paper.

Resistance to inks: This had deteriorated very much compared with the sized but unloaded paper (Expt. 59); ordinary inks ran on the surface, roughened by the absorption of filler, and blotted readily.

Capillary rise in one hour at 20° C.:

Water: 14 mm.

Printing varnish: 6.8 mm.

Colour: Nearly as white as the unsized raw material.

*Expt. 64.*—2% animal glue, 10% of silicate, and 20% of talc.

The glue, silicate, and talc were mixed together in the ordinary way and heated to 80°; the hot mixture was poured into the pulp; afterwards it was precipitated with 10% of crystal alum, as in Expt. 61.

The filtrate and wash water were free from animal glue; even on boiling with tannin no precipitate formed.

The paper contained 16.23% of ash.

From this 16.23% ash 2.43% must be subtracted as the ash of the sized but unweighted paper (Expt. 61) leaving

$16.23 - 2.43 = 13.80\%$  of ignited talc, or  $15.05\%$  unheated talc.

In the paper there was therefore  $15.05\%$  of talc, or  $75.25\%$  of the amount taken.

*Properties of the Paper.*—Strength: The breaking length was 4,467 m., which is about 130 m. less than that of the unsized paper, but is still slightly higher (40 m.) than that of the loaded paper sized with animal glue and aluminium sulphate. The stretch was  $2.61\%$ , which is  $0.16\%$  less than that of the unsized sample.

Handle and rattle: Almost the same as that of the unsized paper.

Capillary rise in one hour at  $20^\circ$ :

Water: 19 mm.

Printing varnish: 6 mm.

Colour: As white as the unsized raw material.

On comparing Expts. 63 and 64 it is seen that, while in Expt. 63 the paper contained  $13.38\%$  of talc ( $= 67\%$  of the amount of talc taken), in Expt. 64 it contained  $15.05\%$  of talc ( $= 75\%$  of the amount of talc taken). Thus, there is an increase of  $8\%$  in the amount of talc fixed in Expt. 64. Sample 64 had also a better handle and rattle and its colour was whiter; the negligible increase of tensile strength need not be considered. Compared with the unsized and unloaded paper (Sample 3D'), the above samples show an increase in the retention of filler of  $10\%$  and  $18\%$  respectively.

**INFLUENCE OF ALUMINIUM HYDROXIDE ON SIZING WITH ANIMAL GLUE.**—The reaction of NaOH with aluminium sulphate to form aluminium hydroxide has been mentioned already in connection with the saponification of fatty acids with sodium hydroxide solution, and the injurious action of aluminium hydroxide with regard to ink resistance has been discussed. The injurious action shows itself also, as might be expected, in the presence of animal size.

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The following experiments were carried out :—

(1) NaOH was made to react in the pulp with aluminium sulphate.

(2) Glue and NaOH were treated with aluminium sulphate in the presence of paper pulp.

*Expt. 65.*—0.5% NaOH with aluminium sulphate.

To 2 litres of pulp (= 50 gm. of air-dried cellulose) 25 gm. NaOH were added in the form of a standard solution, stirred for half an hour and then treated with aluminium sulphate until the reaction was acid. The further procedure was the same as before.

*Properties of the Paper.*—Strength : The breaking length was 4,650 m., about 50 m. higher than that of the unsized paper. The stretch fell by 0.07% to 2.70%.

Handle and rattle : Almost the same as that of the raw material.

Resistance to ink : Ordinary ink ran rather more than on the unsized samples.

Capillary rise in one hour at 20° :

Water : 23 mm.

Printing varnish : 7 mm.

Colour : White like the raw material.

*Expt. 66.*—2% animal glue and 0.5% NaOH with aluminium sulphate.

Animal glue and NaOH were mixed together in the pulp ; precipitation was carried out with aluminium sulphate until the reaction of the pulp was acid.

*Properties of the Paper.*—Here the resistance to ink and the capillary rise are especially important. Ordinary ink ran and blotted badly. On comparison with Sample 59 (precipitation with aluminium sulphate only in conjunction with 2% glue) where ordinary ink scarcely ran at all and only blotted in a few places the unfavourable effect of aluminium hydroxide in relation to ink resistance is brought out clearly. On the other hand, the strength was not influenced unfavourably by the aluminium hydroxide, as is

shown by Expt. 65. It appears likely that the hydroxide acts as a cementing agent.

**SIZING WITH ANIMAL GLUE AND LOADING RICH IN SILICA (TALC).**—Sizing was carried out according to the patent of E. Altmann (p. 80), since he always obtained, in addition to a greater economy in glue, a precipitate of silica or magnesium-hydroxide, or, in the addition patent, of the alkali silicate concerned.

The chief patent reads : “ The method of sizing is characterised by the mixing of a suspension of talc and gelatine with the pulp.”

In an addition patent the process is expanded. The claim reads : “ The method for sizing the pulp is characterised by the mixing of soda with the talc to be used.”

The chief advantages claimed for this method of sizing, besides the increased absorptive capacity of the paper, were the ready absorption of colouring matter by the silica and magnesium hydroxide, and the formation of a protective covering for the colouring matter in the precipitate of silica and consequent avoidance of fading. In the chief patent it was stated as an example that a litre of emulsion should contain 5 gm. of white gelatine and 10 gm. best fine-ground talc, well mixed in hot water at 70°–75°. Five litres of this emulsion mixed with the hot pulp should be sufficient for 100 kilos of printing paper ; a special addition of filler should not be necessary, since the talc of the size itself acts as a loading material.

The additions seem to be extraordinarily small, for they amount to only 0.025% glue and 0.050% talc referred to the air-dried cellulose.

In the subsidiary patent commercial ammonia soda amounting to 30% of the weight of talc is added, the amount added to the pulp, as stated in the original patent, being adjusted accordingly.

The author has carried out experiments with forty times the amounts of animal glue and talc given in the patents, since no effect could be produced by the small additions given above.

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*Expt. 67.*—1% white gelatine and 2% talc. A solution of 0.5 gm. of white gelatine was mixed to a paste with 1 gm. of talc in 100 c.c. of hot water at 75°, and added to the pulp while still hot. After stirring for half an hour the solution was precipitated with aluminium sulphate solution till the pulp was acid.

Only slight traces of precipitate with tannin occurred in the filtrate, even on heating.

*Properties of the Paper.*—Handle and rattle : Very good

Colour : Almost as white as the original material.

Resistance to ink : Standard ink ran to a considerable extent, and showed through in places.

Capillary rise in one hour at 20° :

Water : Mean 20 mm.

Printing varnish : Mean 6 mm.

*Expt. 68.*—1% white gelatine, 2% talc and soda.

The mixture of talc and soda was in the proportion of 7 to 3, and was suspended with the gelatine solution in 100 c.c. of water at 75°. The mixture was added to the pulp, which was then treated with aluminium sulphate solution to give an acid reaction.

Only a slight turbidity was produced by tannin in the filtrate, even on heating.

*Properties of the Paper.*—Handle and rattle : Very good, as in Expt. 67.

Colour : Almost as white as the original material.

Resistance to ink : Standard ink ran, but less than in Expt. 67, since it was absorbed more quickly.

Capillary rise in one hour at 20° :

Water : Mean 17.2 mm.

Printing varnish : Mean 7 mm.

The paper is in no sense "waterproof."

*Expt. 69.*—1% white gelatine with aluminium sulphate. Amounts of pulp and gelatine as in the previous experi-



ments. Addition of tannin to the filtrate before washing gave a slight precipitate which increased on heating.

*Properties of the Paper.*—The colour was dull as compared with samples from 67 and 68. Standard ink ran considerably and penetrated more quickly than with the other two samples.

These last three experiments demonstrate the capacity of talc, thanks to its colloidal structure, to absorb other colloidal substances, such as gelatine. Altmann has thus based his patent on a property of talc which in recent times has also been utilised in other substances for similar purposes.

In the second chapter of this book (Expts. 3A, etc.) mention has already been made of the advantages of talc over china clay as a loading material as regards the strength and stretch of the resulting paper, and it has been pointed out that these advantages are probably due to its powers of absorbing cellulose hydrates, and to the precipitation of magnesium hydroxide and silica from its suspensions.

On examining the numerical results of the various experiments it is seen that in addition to the increase of 22% in the breaking length of paper sized with animal glue over that of unsized paper, the addition of silicate causes a further increase. The same holds for loaded paper. The increased absorption of talc in silicate-gelatine sizing amounts to 32% of the absorption in unsized papers.

Here also the increase in absorptive capacity of the paper, both for aqueous and oily liquids, produced by the addition of silicate is noteworthy, since this factor appears to render such papers peculiarly suitable in practice for rapid printing.

## CHAPTER V

### SILICATE AND STARCH

OF the various methods of paper sizing employing silicate, probably none has received more attention than that which uses a combination of silicate and starch. One such investigation on this subject is that of Hans Wrede ("W.-Bl. f. P." 1913, No. 10, p. 835). In the fifth of his seven recommendations on the application of starch and silicate, the author refers to the "Mineral Starch-sizing" of printing paper. In this connection he draws special attention to the fact that in these papers the important point is the readiness with which the paper will absorb oil printing inks. Wrede used about 3.5% to 5% of silicate and an equal quantity of starch, left both to swell up together, added the warm mixture to the Hollander, and precipitated it with aluminium sulphate till the reaction was acid. According to his statements a loss of 30% to 40% of the starch occurs. E. Fues, on the other hand, obtained a practically quantitative precipitation of starch by very careful neutralisation with aluminium sulphate. On drying the precipitate of aluminium silicate Wrede obtained a white powder, while on drying the precipitate produced by adding aluminium sulphate to silicate and starch a horny mass results.

Mention may here be made of the later work of Alfred Lutz\* on the influence of starch sizing upon the quality of the paper. The author proves that the absorption of starch by the paper amounts to 73.2% of the mass taken for raw mixed starch and to only 46.2% for starch paste.

In the sizing carried out by us the starch in the waste liquor was not estimated, since here the main point is the strengthening of the paper by silicic acid, and the influence

\* *Ber. d. Hauptvers. d. Vereins d. Zellstoff und Papierchemiker*, 1907.

of the latter on the properties of paper sized with silicate and starch.

The following introductory experiments were first carried out.

**PRECIPITATION EXPERIMENTS WITH STARCH PASTE WITHOUT FIBRE.**—5 gm. of potato starch in 200 c.c. of distilled water were heated on a water bath at 65° till swollen.

(1) Half this solution was added to  $\frac{1}{2}$  litre of tap water in a tall cylinder. The starch appeared in quite finely-divided flakes, but these remained in suspension. On adding 1 c.c. of 10% aluminium sulphate solution (= 0.1 gm. crystalline sulphate) a thick flocculent gelatinous mass was formed which quickly settled out as a bulky precipitate. The remaining liquid gave a faintly acid reaction. On filtering, the precipitate remained behind as a jelly on the filter, and the filtrate was clear.

(2) The other half of the starch solution was treated, undiluted, with 1 c.c. of 10% aluminium sulphate solution; it showed no appreciable precipitate. On the addition of a further 9 c.c. of aluminium sulphate solution a finely-divided and very voluminous precipitate settled out. The filtering took a long time as the precipitate clogged the filter. The first experiment was performed again in cylinders with 2 litres of tap water, as in the sizing.

(a) 2.5 gm. of soaked starch, corresponding to 5% of sizing material on the weight of pulp, gave after some time a fine flocculent precipitate which settled out at once. This was filtered off and dried. The clear filtrate again gave an abundant starch precipitate with aluminium sulphate.

It is therefore necessary to proceed still further with the dilution, which in some cases amounted to 1 in 800, in order to obtain complete precipitation of the starch. This also corresponds with the observations of Lutz (see above), who recommends the use of an amount of water equal to 2,000 to 2,500 times the weight of starch in preparing sheets weighing 100 to 110 gm. per metre with 5% starch sizing.

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(b) In a second case 2.5 gm. of swollen starch, corresponding to a 5% starch sizing, were mixed with 2,000 c.c. of tap water, and a few cubic centimetres of aluminium sulphate solution added. In this case there was formed a thick flocculent precipitate of starch which was filtered and dried.

(c) 5 gm. of potato starch were heated with 200 c.c. water and 5 gm. of silicate solution (38° Bé.) on a water bath at 65° C. till swollen.

One half of the solution in 2 litres of tap water gave a flocculent precipitate as above; the filtrate in this case also gave a further precipitate with aluminium sulphate.

The other half was treated with aluminium sulphate solution in 2 litres of tap water till the reaction was faintly acid; the resulting precipitate was filtered and dried.

*Comparison of the Dried Precipitates.*—(a) Starch paste alone precipitated by dilution gave a white powder.

(b) Starch paste precipitated with aluminium sulphate gave a clear horny mass with considerable diminution of volume.

(c) Starch swollen with silicate and precipitated with aluminium sulphate, contracted in a similar manner to a dark-yellow horny mass. In this last case we have a confirmation of Wrede's observations (see above).

According to these experiments the precipitates (b) and (c) are those to be desired for the sizing of paper.

Systematic sizing experiments and comparison of results were now carried out.

Potato starch was used in all cases as being the cheapest.

**SIZING WITH SWOLLEN STARCH.**—*Expt. 70.*—5 gm. swollen potato starch.

Two litres of pulp (= 50 gm. of air-dried cellulose) were stirred with 2.5 gm. of potato starch, previously swollen on a water bath at 65°. After stirring for one hour the mixture was filtered and washed, and then sampled at a dilution of 1 in 1,000.

*Waste Liquor.*—Fairly clear.

*Properties of the Paper.*—Strength: the breaking length

was increased by 350 m. over that of the unsized paper to 4,150 m.

The stretch was 3.76%, an actual increase of 0.08%.

Handle and rattle: The rattle is better than that of unsized paper; the handle is more substantial.

Colour: Dull white.

Capillary rise in one hour at 20° C.:

Water: 30.3 mm.

Printing varnish: 7 mm.

*Expt. 71.*—5% potato starch paste precipitated with aluminium sulphate till the reaction of the pulp is acid.

The weights of pulp and starch were exactly as in Expt. 70, but after standing for half an hour 18 c.c. of 10% aluminium sulphate solution were added, i.e., 3.6% crystal alum referred to the air-dried pulp. The reaction of the pulp was then acid.

*Waste Liquor.*—Fairly clear.

*Properties of the Paper.*—Strength: The breaking length increased to 4,350 m., higher by 200 m. than in the case of the 5% starch sizing without aluminium sulphate, and 550 m. higher than that of the unsized paper.

The stretch was 3.40%, a drop of 0.36% and 0.20% respectively.

Handle and rattle: The rattle was still better than in the last experiment. The handle was substantial.

Capillary rise in one hour at 20° C.:

Water: 28 mm.

Printing varnish: 6 mm.

Colour: Yellowish white, duller than in Expt. 70.

The paper was incinerated with the object of estimating the amount of filter later. The ash was found to amount to 0.78%.

The ash content of the unsized and unweighted paper amounted only to 0.42%, so that through the starch sizing the ash content is raised by 0.36%, i.e., an increase of ash of 86%.

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*Expt. 72.*—10% swollen starch precipitated with aluminium sulphate till reaction is neutral.

The usual amount of pulp was mixed with 5 gm. of potato starch, swollen on a water bath at 65°, and after stirring for half an hour was precipitated with 7 c.c. aluminium sulphate, *i.e.*, 1.4% crystal alum referred to air-dried pulp (till reaction was neutral).

*Waste Liquor.*—Fairly clear; after filtration a small amount was treated in a test tube with boiling  $\text{BaCl}_2$  solution; only a trace of barium sulphate appeared, so that no alumina can have passed into the waste liquor.

*Properties of the Paper.*—Strength: The breaking length rose to 4,580 m., 750 m. higher than in the unsized paper and 200 m. higher than in the feebly acid 5% starch sizing.

The stretch rose to 3.80%, 12% higher than for the unsized sample.

Handle and rattle: Rattle very good; handle very full and substantial.

Capillary rise in one hour at 20° C.

Water: 24 mm.

Printing varnish: 6.5 mm.

Colour: Yellowish white.

The paper was incinerated with the object of determining the absorption of loading in a later experiment. The ash amounted to 1.10%.

The ash content of the paper sized with 10% starch is increased to 1.10% or 0.32% over that of the 5% starch sized paper, *i.e.*, an increase of ash of 41%; and by 0.68% over that of the unsized paper, *i.e.*, an increase of ash of 162%.

**SIZING WITH SILICATE IN CONJUNCTION WITH SWOLLEN STARCH.**—*Expt. 73.*—5% swollen starch and 5% water glass (38° Bé.) were added separately. Neutral precipitation.

The quantities of pulp and starch were as in *Expt. 71*. Shortly after the starch 5% water glass of 38° Bé was added, to the pulp and after stirring for half an hour was precipi-

tated with 24% crystalline aluminium sulphate, referred to air-dried cellulose (till reaction was neutral).

*Waste Liquor.*—Slightly turbid. Analysis of the waste liquor gave 0.4570 gm.  $\text{SiO}_2$ . The amount originally added was 0.6550 gm., so that 70 % has passed into the water and 30% into the pulp.

The absorption of silicic acid thus amounts to 0.4%, referred to the air-dried pulp.

This small absorption is obviously due to the neutral precipitation as has already been shown in the precipitation and solution experiments of Chapter I. of this work.

According to E. Fues the starch should be taken up almost quantitatively.

*Properties of the Paper.*—Handle and rattle were very good, the paper, however, felt harder than in the sizing without silicate. The colour was yellowish white.

*Expt. 74.*—5% swollen starch and 10% silicate added separately. The quantities of pulp and starch were the same as in the last experiment, but 10% instead of 5% silicate was added soon after the starch, and was then precipitated with 4.2% crystal alum (till the reaction was just acid).

*Waste Liquor.*—Slightly turbid.

*Properties of the Paper.*—Handle and rattle: Rattle was distinctly better than in the last experiment, and in that without silicate. The handle was more substantial and harder than in the two previous experiments.

Colour: Yellowish white, but brighter than when sized without silicate, though the alkaline starch usually gives the paper a more distinctly yellow colour.

Capillary rise in one hour at 20° C.

Water: 32 mm.

Printing varnish: 8 mm.

*Expt. 75.*—10% raw starch and 10% silicate (38° Bé). Starch powder, mixed with cold water to a homogeneous paste, was added to 2 litres of pulp = 50 gm. air-dried cellulose, and then treated with 10% silicate of 38° Bé;

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the whole was stirred for half an hour and then precipitated with 4% crystal alum till the pulp was acid.

*Waste Liquor.*—Milky.

*Properties of the Paper.*—Strength : The breaking length was 4,300 m., 650 m. higher than that of the unsized sample. The stretch was raised by 0.35% to 3.5%.

Handle and rattle : The rattle of the paper was good and the handle was substantial.

Capillary rise in one hour at 20° C. :

Water : 33 mm.

Printing varnish : 7.6 mm.

Colour : The colour was spoilt by the fact that the tap water was yellow. It cannot therefore be taken into account.

In the previous experiments the silicate was mixed in the pulp which already contained the starch ; in the next experiments the starch was allowed to swell up with the silicate, and the alkaline starch mixed with the silicate, then added to the pulp.

SIZING WITH STARCH SWOLLEN WITH SILICATE.—*Expt. 76.*  
—5% potato starch swollen with 5% silicate.

To the usual amount of pulp were added 2.5 gm. of starch which had been heated with 2.5 gm. of silicate on the water bath in a total volume of 200 c.c. at 65° C. till swollen ; after stirring for half an hour 2.4% crystal alum was added till the reaction of the pulp was neutral. The pulp was filtered, washed and sampled as before.

*Examination of Waste Liquor.*—The waste liquor was slightly turbid.

It was found to contain 0.4831 gm.  $\text{SiO}_2$ .

The amount added at first was 0.6550 gm., and thus 74% of the silica has passed into the waste liquor and 26% into the pulp, which means an absorption of 0.34% of silicic acid, referred to the air-dried cellulose. The absorption of silicic acid was thus somewhat lower than in Expt. 73, where the silicate and starch were added separately.

*Properties of the Paper.*—The breaking length was 4,280 m.,



630 m. higher than that of the sample sized only with 5% starch in Expt. 71. The extension was 3.67%, a higher value than in the unsized paper.

Handle and rattle : Very good ; the paper felt substantial, but rather harder than the sample sized with starch in the absence of silicate (Expt. 71).

Colour : Nearly that of the bleached raw material, although the alkaline starch produces a stronger yellow tint and turbidity in the paper.

An ash determination was carried out in order to calculate the amount of loading absorbed in later experiments, and gave a figure of 0.955% ash.

In the following experiment aluminium sulphate solution was added till the reaction was acid in order to obtain a larger absorption of silicic acid, as the experiments on solution and precipitation in Chapter I. would lead one to expect. The neutral precipitation had been employed in order to obtain a better absorption of potato starch as already mentioned.

*Expt. 77.*—5% potato starch swollen with 10% silicate. The amounts of pulp and starch were the same as in the last experiment, but the starch was heated at 65° till swollen with 10% silicate (38° Bé.) referred to air-dried pulp. It was precipitated with 5% crystal alum, referred to air-dried cellulose, i.e., till the reaction of the pulp was strongly acid.

*Examination of the Waste Liquor.*—The waste liquor was almost clear and contained 0.5359 gm.  $\text{SiO}_2$ . The original amount of silicate contained 1.3100 gm.  $\text{SiO}_2$  and therefore 41% of the silicic acid has passed into the waste liquor.

This corresponds to an absorption of 1.58% silicic acid, referred to air-dried cellulose.

This absorption of 59% of the amount of silicic acid taken is no less than 19% and 23% greater than for the neutral precipitates in Expts. 73 and 76 respectively ; nevertheless in the following experiments precipitation was carried

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out only to neutrality on the ground that the starch, as the dearer of the two sizing materials, should especially be retained, provided that there is a sufficiency of silicic acid.

*Properties of the Paper.*—Besides good rattle and substantial handle the colour is only slightly lower than in the unsized sample.

Capillary rise in one hour at 20° C. :

Water : 26 mm.

Printing varnish : 7.5 mm.

*Expt 78.*—5% starch swollen with 10% silicate (38° Bé). Amounts of pulp, starch and silicate as in the previous experiment ; but precipitated with 4% aluminium sulphate, i.e., till the reaction is practically neutral.

*Waste Liquor.*—Slightly turbid.

*Properties of the Paper.*—Except for the firmer handle, which is explained by a larger absorption of starch, due to the precipitation being carried to neutrality, no appreciable difference from sample 77 could be noticed.

The amount of starch was now increased to 10%, referred to air-dried cellulose, since Lutz in the work quoted above found an appreciable increase in the strength of the paper when the percentage of starch was raised to this figure.

*Expt. 79.*—10% starch swollen with 10% silicate.

5 gm. potato-starch were heated with 5 gm. of silicate at 65° till swollen and added to 2 litres of pulp (= 50 gm. of air-dried cellulose). After stirring for half an hour 4.2% crystal alum was added (i.e., till practically neutral) and the pulp worked up further as usual.

*Waste Liquor.*—Slightly turbid.

*Properties of the Paper.*—The ash content amounted to 1.92%.

\*Strength: The breaking length was 4,600 m., 950 m. higher than that of the unsized paper and 200 m. higher than that of the paper sized with 10% starch paste alone (Expt. 72). The breaking length is 300 m. higher than

in the case of the paper sized with 10% starch in conjunction with 10% silicate (Expt. 75).

• Handle and rattle : Very good ; handle is harder also than in sample 72.

Capillary rise in one hour at 20° C. :

Water : 36 mm.

Printing varnish : 6.66 mm.

Colour : Yellowish white ; paler than in sample 72.

The increased strength in the last papers, compared with paper not sized with silicate, is probably only due to the formation of alkaline starch in the process of swelling with silicate. In order to see to what extent the silicic acid precipitate is responsible for this increase, an experiment was carried out using the same amount of starch, which was swollen by heating with as much alkali as corresponds to the 10% silicate in the above experiment.

100 gm. silicate (38° Bé.) were equivalent according to analysis to 7.95 gm. = 11 gm. NaOH approximately.

5 gm. of silicate (38° Bé.) are therefore equivalent to 0.55 gm. NaOH = 14 c.c. N. NaOH solution.

5 gm. of potato-starch were accordingly heated with 14 c.c. N. NaOH solution in a total volume of 200 c.c. on a water bath at 65°.

The precipitates of this alkaline starch solution in 2 litres of tap water were similar to those observed in the beginning of this section with starch and silicate pastes ; the only discernible difference was that the pure alkaline starch was more gelatinous than similar masses of silicate and starch pastes. The following experiment was then carried out :

*Expt. 80.*—10% starch with alkali corresponding to 10% silicate. The usual weight of pulp was mixed with 5 gm. of potato-starch, swollen at 65° with 14 c.c. N. NaOH solution as described above and precipitated in the usual way with aluminium sulphate solution till the reaction was almost neutral.

*Waste Liquors.*—Slightly turbid.

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*Properties of the Paper.*—Strength: The breaking length was 4,400 m. which is only 750 m. above that of the unsized sample, so the increase remained the same as in the paper sized with pure 10% starch paste (sample 72) but the breaking length was lower than in the case of paper sized with silicate and starch (sample 79). The stretch was 4%, an increase of 0.2% and 0.52% over samples 72 and 79 respectively, and of 0.85% over the unsized sample.

Handle and rattle: Very good. The surface felt greasy.

Colour: Yellowish white, duller than sample 79.

Capillary rise in one hour at 20° C.:

Water: 36 mm.

Printing varnish: 6.83 mm.

A comparison of the preceding sizing experiments shows that the increase of breaking length over that of the unsized paper is nearly 27% greater in the case of paper sized with silicate and starch than in that of paper sized with pure alkaline starch; this is obviously due to the action of the silicic acid precipitate.

The figure for stretch in the last experiment is indeed higher, but in hand-made paper too much importance must not be attached to the stretch value.

In the following experiments the absorption of filling materials by paper sized with silicate and starch and with starch alone was investigated.

*Expt. 81.*—5% starch swollen with 5% silicate and 20% china clay added. The starch and silicate, swollen in the usual way at 65°, were added to 2 litres of pulp and 10 gm. of china clay were added at once; after stirring for half an hour precipitation was carried out with 2.4 % crystal alum, i.e., till reaction was almost neutral.

*Waste Liquor.*—Milky; due to the presence of a suspension of the filling material.

*Estimation of Filling Material.*—An ash determination on the loaded paper gave 13.04% ash.

According to the incineration of sample 76, out of this 13.04% of ash 0.96% is the ash of sized paper; therefore there is 12.08% of ignited china clay, or 13.98% of actual china clay.

The paper therefore contains 70% of the amount of china clay taken.

*Properties of the Paper.*—Handle and rattle: As good as in the unsized and unweighted paper, but the handle is much more substantial.

Colour: Nearly as white as the bleached raw material.

Capillary rise in one hour at 20° C.:

Water: 37 mm.

Printing varnish: 7 mm.

*Expt. 82.*—5% swollen starch with 20% china clay added. Amounts of pulp and starch as in Expt. 71. Shortly after the addition of the starch paste, 10 gm. of china clay were washed into the pulp; after stirring for half an hour precipitation was carried out with 1.5% crystal alum, i.e., till reaction was practically neutral.

*Waste Liquor.*—Milky, due to the presence of loading.

Capillary rise in one hour at 20° C.:

Water: 35 mm.

Printing varnish: 7 mm.

*Estimation of Loading.*—The loaded paper contained 11.43% ash. Subtracting from this 0.78% for the ash of the unloaded paper the amount of ignited china clay is 10.65%, corresponding to 12.20% of actual china clay.

The paper therefore contains 61% of the loading taken.

*Properties of the Paper.*—Handle and Rattle: Not quite so good as in Expt. 81. The colour is the same. These two experiments show that by the application of silicate the fixation of loading by the pulp is increased by 9% of the weight of loading taken; that is an increase of about 15% in the absorption of china clay.

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In the following table the fixation of loading in the present experiment is compared with that obtained with unsized paper, and with paper treated only with aluminium sulphate solution.

Sample	3c'	.	.	.	47% fixation.
"	3c''	.	.	.	50% "
"	82	.	.	.	61% "
"	81	.	.	.	70% "

The increased fixation of loading by the pulp amounts to 14% in sample 82 and 23% in sample 81 as compared with the unweighted and unsized paper, that is an increase of absorption of 30% and 49% respectively on the china clay used.

In the following experiments the absorption of talc by paper sized with silicate and starch and with plain starch paste was investigated.

*Expt. 83.*—10% starch swollen with 10% silicate, with 20% talc added.

5 gm. of potato-starch, swollen with 5 gm. of silicate (38° Bé.) at 65° C., were added to the pulp; 10 gm. of talc were washed in at once and after half an hour's vigorous stirring precipitation was carried out with 4.2% crystal alum till the reaction was almost neutral.

*Waste Liquor.*—Nearly clear.

*Properties of the Paper.*—In spite of the high ash content the paper has good rattle and substantial handle. The colour is as white as in the bleached raw material.

*Estimation of Loading.*—An estimation of the ash gave 17.14%.

Since the ash of the unloaded paper is 1.92% (sample 79), the present sample contains 15.22% of ignited talc, that is, 16.59 % of talc before heating.

The paper therefore contains 83% of the mass taken.

*Expt. 84.*—10% of swollen starch with 20% of talc added.

The amounts of pulp and starch were as in *Expt. 72*; shortly after the addition of the starch paste 10 gm. of talc

were washed into the pulp; after stirring for half an hour precipitation was carried out with 1.4% crystal alum, referred to the air-dried pulp, i.e., till the reaction was nearly neutral.

*Waste Liquor.*—Almost clear.

*Properties of the Paper.*—The rattle is rather less good than in the previous experiment: handle and colour are similar.

*Estimation of Loading.*—The ash amounted to 14.66%.

Subtracting 1.10% for the ash of the unloaded paper (sample 72) gives 13.56% of ignited talc, or 14.78 % of talc before heating.

The paper therefore contained 74% of the amount of loading taken.

The increased absorption of talc by the pulp in the paper sized with silicate and starch therefore amounted to 9% over the absorption when the paper was sized with raw starch paste, that is a 12% increase in the loading.

In comparison with these results are set out below the talc fixation of unsized paper and of paper treated with aluminium sulphate only (Chapter I., sample 3D' and 3D'').

Sample	3D'	.	.	.	57% absorption
„	3D''	.	.	.	61% „
„	84	.	.	.	74% „
„	83	.	.	.	83% „

The increase of loading over that in the unsized and unweighted paper amounts to 17% for the paper sized with starch paste and to 26% for that sized with silicate and starch.

**SUMMARY OF STARCH-SIZING EXPERIMENTS.**—A comparison of the numerical values for paper sized with silicate and starch with those for paper sized by other methods shows the increased tensile strength of paper sized with silicate and starch, as compared with the values for paper sized with raw starch, although these are already high.

The increases in the amount of loading absorbed in the silicate combinations are 15% and 12% for china clay and

talé respectively, compared with the amounts retained in the paper sized with starch alone ; thus the total absorptions of mineral loading are 49% and 46% respectively higher than in the unsized and unloaded paper. This fact, together with the excellent handle and rattle produced, justifies the use of potato-starch with silicate, in spite of its cost.



## CHAPTER VI

### SILICATE AND CASEIN

IN order to complete the series of sizing experiments with silicate, the latter was also used in conjunction with casein.

Two solutions were prepared :—

(a) 5 gm. casein were swollen with water and dissolved with just sufficient ammonia, at a gentle heat of  $40^{\circ}$ , and made up to 500 c.c. The amount of ammonia required had been previously determined.

(b) 5 gm. of casein were likewise swollen with water and dissolved with 10 c.c. of silicate ( $1 : 4 = 2.5$  gm. silicate of  $38^{\circ}$  Bé.) at a gentle heat of  $40^{\circ}$  on a water bath, 90 c.c. more silicate were added, and the whole made up to exactly 500 c.c. The solution thus contained 5 gm. of casein and 25 gm. of water glass of  $38^{\circ}$  Bé.

Both sizing solutions had the fresh smell of good casein and were worked up in succession; the solutions were pale yellow in colour and slightly cloudy.

SIZING WITH CASEIN IN AMMONIACAL SOLUTION IN CONJUNCTION WITH SILICATE.—*Expt.* 85.—1% casein in  $\text{NH}_3$  solution and 5% silicate of  $38^{\circ}$  Bé.

Two litres of pulp (= 50 gm. air-dried cellulose) were treated with 50 c.c. of casein solution (a) ( $= \frac{1}{2}$  gm. casein) and then with 5% silicate of  $38^{\circ}$  Bé. diluted to 1 in 4. It was then stirred for half an hour and precipitated with aluminium sulphate, till the reaction was neutral, with 10 c.c. of 10% aluminium sulphate solution (i.e., 2% crystal alum referred to air-dried cellulose). After a further half hour it was filtered, washed and sampled.

*Waste Liquor.*—Turbid and opalescent.

*Examination of Waste Liquor.*—0.6070 gm.  $\text{SiO}_2$  was found

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in the waste liquor. The 2.5 gm. of silicate used contained 0.655 gm.  $\text{SiO}_2$ , and therefore 93% of the  $\text{SiO}_2$  has passed into the liquor, only 7% remaining in the pulp.

Referred to air-dried cellulose this is an absorption of only 0.1%  $\text{SiO}_2$ .

*Properties of the Paper.*—Handle and rattle: The rattle is the same as in the unsized raw material; the handle is fuller, more voluminous and softer on the surface than in the unsized sample.

Colour: Whiter than the bleached unsized raw material.

Capillary rise in one hour at  $20^\circ \text{C}$ . :

Water: 46 mm.

Printing varnish: 8 mm.

*Expt. 86.*—1% casein dissolved with ammonia and 5% silicate of  $38^\circ \text{Bé}$ .

The weights of pulp, casein, and silicate were the same as in the previous experiment, but precipitation was produced with a large excess (6%) of crystalline aluminium sulphate (compared with 2% previously used) till the reaction was strongly acid.

*Waste Liquor.*—Very cloudy.

*Examination of Waste Liquor.*—0.6545 gm.  $\text{SiO}_2$  was found in the waste liquor, as against 0.6550 gm. originally taken. Therefore there is 99.8% of the  $\text{SiO}_2$  in the waste liquor and only 0.2% in the pulp.

In the experiments in Chapter I. (Expts. 3 and 3B) it was definitely shown that in strongly acid precipitation less silicic acid was retained in the pulp. Moreover in Expts. 85 and 86 the amounts of aluminium sulphate represented extreme cases (in the first the lower, in the second the upper limit); with some quantity between the two there would probably be a better absorption.

*Properties of the Paper.*—Handle and rattle: The same as for the unsized sample.

Colour: Just as in the unsized raw material.

Capillary rise in one hour at 20° C. :

Water : 25 mm.

Printing varnish : 7 mm.

It appears also that not much of the casein remains in the pulp, for in contrast to sample 85 this paper had only the same qualities as the unsized raw material. The very cloudy waste liquor also points to a large loss of casein.

SIZING WITH CASEIN IN SILICATE SOLUTION.—*Expt. 87.*—1% casein dissolved with 5% silicate (38° Bé.).

Quantities of pulp as before ; 50 c.c. of sizing solution (*b*) (i.e., 1 gm. of casein and 2.5 gm. of 38° Bé. silicate) were added to the pulp and precipitation produced with 2% crystal alum.

*Examination of Waste Liquor.*—The waste liquor was cloudy and opalescent.

In the waste liquor there was found 0.5961 gm.  $\text{SiO}_2$ .

Since the amount originally taken was 0.6550 gm., 91% of the silicic acid has passed into the waste liquor, and 9% into the pulp.

Referred to air-dried cellulose this amounts to an absorption of 0.12%  $\text{SiO}_2$ .

*Properties of the Paper.*—These correspond to those found in the first experiment of this chapter. (*Expt. 85*) : the breaking length was 4,000 m., or 350 m. better than for the unsized paper. The stretch was 3.60%, 0.54% higher than in the unsized paper. For the purpose of estimating the amount of loading present in the following experiments, the ash of this paper was estimated and found to be 0.57%.

These lower ash values also point to the low content of  $\text{SiO}_2$  ; the ash of the cellulose alone amounts to 0.42%.

*Expt. 88.*—5% casein dissolved with 25% silicate.

This uneconomical sizing experiment was carried out with 50 gm. of pulp and half of the sizing solution (*b*) (2.5 gm. of casein and 12.5 gm. of silicate of 38° Bé.). Precipitation was effected with 40 c.c. of 10% aluminium sulphate

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solution, i.e., 8% crystal alum referred to air-dried cellulose.

*Waste Liquor.*—Milky and turbid.

*Properties of the Paper.*—Handle and rattle: The rattle of the paper was very good, but it felt hard and it lacked the substance of the sample sized with 1% casein and 5% silicate.

Colour: Whiter than the unsized raw material.

Capillary rise in one hour at 20° C.:

Water: 15 mm.

Printing varnish: 6 mm.

*Expt. 89.*—1% casein dissolved with 5% silicate and with the addition of 20% china clay.

Quantities of pulp, casein and silicate as in Expt. 87. Shortly after the addition of the sizing solution 10 gm. of china clay, made into a paste, were added to the pulp; precipitation with aluminium sulphate was continued till the reaction was slightly acid.

*Waste Liquor.*—Turbid.

*Properties of the Paper.*—Handle and rattle: Rattle almost the same as in the unsized and unweighted sample: handle not quite so substantial as in the corresponding sized but unweighted sample.

Colour: Almost as white as the bleached and unsized raw material.

Capillary rise in one hour at 20° C.:

Water: 23 mm.

Printing varnish: 7 mm.

*Estimation of Loading.*—The ash amounted to 11.96%. After subtracting the ash of the unloaded paper this leaves 11.38% of ignited china clay, or 13.16% of actual china clay before ignition. The paper thus contains about 66% of the amount of filler taken.

*Expt. 90.*—1% of casein dissolved with ammonia and 20% of china clay.

To the usual amount of pulp were added 50 c.c. of the sizing solution (a) ( $= \frac{1}{2}$  gm. of casein) and immediately afterwards 10 gm. of china clay. After standing for half an hour precipitation was carried out with aluminium sulphate till reaction was slightly acid.

*Waste Liquor*.—Cloudy.

*Properties of the Paper*.—Handle and rattle: Rattle slightly less good than in the above experiment, and also in the unsized sample; but the handle is more substantial than in the preceding experiment.

*Colour*: Rather duller than in the last sample.

*Estimation of Loading*.—The ash amounted to 9.47%, corresponding to  $(9.47 - 0.42) = 9.05\%$  of ignited china clay; it is assumed here that the ash of the sized unloaded paper is the same as that of the unsized raw material.

9.05% of ignited china clay corresponds to 10.46% of actual china clay and thus the paper had absorbed 52% of the filler.

A comparison of the last two experiments, one using silicate and casein, and the other casein alone, shows that the former produces not only a better rattle and paler colour, but also an increase of loading content, in this case from 52% to 66%, a rise of 14% of china clay, i.e., an increase of 27% in the amount of china clay absorbed.

A comparison is also given of the absorption of loading in the present experiments with that obtained with unsized paper and with paper treated only with aluminium sulphate (Chapter I., Expts. 3c' and 3c'').

Sample 3c'	47% absorption.
„ 3c''	50% „
„ 90	52% „
„ 89	66% „

The increase of loading in sample 90 amounts only to 5%, but in sample 89 (silicate combination) to 19% compared with the loaded and unsized paper (sample 3c').

The waste liquor from experiment 89 was not examined

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for  $\text{SiO}_2$ , yet one can conclude from the properties of the weighted paper that there is a larger content of  $\text{SiO}_2$  than in the neutral sizing (Expt. 87) and the similar strongly acid precipitation (Expt. 86).

Apart from the high price of casein, its combination with water glass does not seem to be very satisfactory where a sizing is carried out in the pulp. If the sizing were carried out by treating the raw material with silicate and then painting the paper with casein, the results might possibly be more promising; the large capillary rise shown by paper sized with silicate will certainly ensure a good penetration of casein; the handle and rattle also are likely to remain almost the same in the painted art printing paper.

The good capillary rise for water and printing varnish is particularly noticeable in paper sized with silicate and casein.

## CHAPTER VII

### SUMMARY

THE foregoing records demonstrate the advantages of silicate sizing and of sizings in which the silicate is used in conjunction with other colloidal materials.

The greater strength and considerably higher fixation of mineral loading in the case of silicate sizing is clearly shown. All the papers sized with silicate have also better handle and rattle, even when more heavily loaded. The large capillary rise for oily liquids, and the speed with which they are absorbed is of great importance as regards the suitability of the paper for printing, and particularly for rapid printing processes. With paper sized with silicate, the smooth surface produces a more plastic and sharply defined imprint, which is of particular importance for so-called surface printing. A further advantage is the decreased tendency to yellowing in papers made from unbleached pulp, or from pulp containing rosin size in addition to the silicate.

Silicate sizing is also of importance in facilitating the working of the paper machine. Papers thus treated work very freely at the press rolls, are easily removed from the wires, and are readily dehydrated at the suction boxes. As regards the recovery of material from the wash waters, the silicate content assists the precipitation of filling materials and fine fibres, even though these are present only in small quantities.

To all these good qualities must be added the relatively smaller cost of the silicate.

The foregoing work demonstrates clearly that for many printing papers sizing with rosin may be entirely dispensed with, even to the last fractional proportions supposed to be necessary; in the case of papers for rapid printing, they are

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rather harmful. Silicate sizing in this most important class of papers not only serves the same purposes, but actually excels resinous or fatty sizes in all the essential technical effects.

Silicate sizing is also effective in the case of papers which are engine coloured with dye-stuffs. The absorption of colouring matter is increased by the absorptive capacity of silicic acid, and in addition the precipitation of silicic acid forms a protective coating round the particles of colour, thereby retarding the fading of very fugitive tints.

The chief advantages of silicate sizing may again be summarised as follows :—

- (1) Good working on the paper machine.
- (2) No sticking at the presses.
- (3) As a result of (1) and (2), smaller consumption of felts.
- (4) Rapid and complete sedimentation of the machine water.
- (5) Increased strength.
- (6) Better handle and rattle to the paper.
- (7) Higher fixation of loading while retaining the handle of the paper.
- (8) Large capillary rise for oils and a smooth surface (printing qualities).
- (9) Flatness of cut sheets of the paper.
- (10) Increased absorption and fixation of dye-stuffs.